This is to certify that Mr WILLIAM S. REID has successfully sustained an oral examination on the subject matter of his thesis by a committee of the Department of Chemistry.

Members
of
Committee.

October 1937.

LINEAR RELATIONSHIPS BETWEEN THE HEAT, FREE ENERGY, AND ENTROPY OF SOLVATION.

by

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CONTENTS

INTRODUCTION

Various attempts have been made to discover a general law obeyed by all solutions, but no single theory as yet advanced explains all solubility phenomena.

Last century, three empirical laws were formulated. Henry (Phil. Trans. 29, 1803; Gilb. Ann., 20, 147, 1805) studied the solubility of gases in liquids, and discovered that the amount of gas dissolving in a given volume of the solvent was proportional to the partial pressure of that gas above the solution.

If we express the solubility of the gas in terms of mol fraction, we obtain the relation,

$$\frac{p_2}{N_2} = K, \qquad (1)$$

where p_2 = partial pressure of the gas,

N_2 = its mol fraction in the liquid,

and K = Henry's Law constant.

Van't Hoff (Phil. Mag., 3 , 157, 1888) stated that

the osmotic pressure of a solution, measured against the pure solvent, is numerically equal to the pressure which the solute would exert as an ideal gas under the same conditions; so that

$$\pi V = n_2 RT, \qquad (2)$$

where π = Osmotic Pressure of solution,

V = Volume of solution,

n_2 = Number of mols of solute,

T = Absolute Temperature,

and R = Ideal Gas constant.

On a firmer theoretical basis is the Law of Raoult, (Compt. rend., 104, 1430, 1887; Z. physik. Chem., 2, 353, 1888), namely, that the fractional lowering of the vapour pressure of a solvent on the addition of an involatile solute equals the mol fraction of the solute at small concentrations; that is,

$$\frac{p_1^\circ - p_1}{p_1^\circ} = N_2, \qquad (3)$$

where p_1° = vapour pressure of pure solvent,

p_1 = vapour pressure of solution,

and N_2 = mol fraction of solute.

Or, since $N_2 = 1 - N_1$,

$$p_1/p_1^\circ = N_1, \qquad (4)$$

where N_1 = mol fraction of solvent.

Similarly, the relation

$$p_2/p_2^\circ = N_2 \qquad (5)$$

holds for the other component.

Though the laws of van't Hoff and Raoult become identical at infinite dilution, in concentrated solutions the identity fails, and modern theories of solubility are founded on Raoult's law and the deviations therefrom.

Zawidzki (Z. physik. Chem., 35, 129, 1900) found that, for certain binary solutions, Raoult's law was true for both components over the whole range of concentrations, that is,

that $\frac{p_1}{p_1^\circ N_1} = 1$

and $\frac{p_2}{p_2^\circ N_2} = 1$, for these solutions.

G. N. Lewis (J.A.C.S., 30, 668, 1908) postulated that such solutions be defined as ideal solutions.

Provided the mol fractions are evaluated properly, it can be shown that Raoult's law is universally true for the solvent for very small concentrations of the solute, and, from thermodynamic principles, it follows that, if Raoult's law holds under these conditions, Henry's law is valid too. (Butler's Fundamentals of Chemical Thermodynamics, vol. II, p. 83).

And so, by comparison of equations (1) and (5), it follows that the constant of Henry's law, is

$$K = p_2^\circ.$$

In general, however, this is not true. Most systems show deviations from Raoult's law, so that the Henry's law constant (that is, the ratio of partial pressure to mol fraction in a very dilute solution), does not coincide with the vapour pressure of the pure liquid.

Generally, then, $p_2/p_2^\circ N_2 = f$, an activity coefficient which is unity for an ideal solution.

Thus, for sufficiently dilute solutions, Henry's law is a general law, and the identification of Henry's law constant K, with p_2° is a special case valid only for ideal solutions.

Generally it may be stated that Raoult's law is valid when the energy and nature of the interaction of the solute molecule with its surrounding molecules shall be the same in the solution as in the pure liquid.

In general, this can be satisfied only when a solvent molecule may be replaced by a solute molecule without change of volume, and when the interaction energy between solvent and solute molecules, is identical with that between two solute molecules.

In particular, Hildebrand ("Solubility" (1924, pp. 60-62) has pointed out that, if, when the pure liquids are mixed, there is (1) no heat effect, and (2) no volume change, Raoult's law is probably valid. But these conditions are not sufficient in all cases to ensure the

validity of Raoult's law. When solute and solvent differ considerably in polar character, there will probably be large heat effects, and so large deviations.

To account for these deviations, Dolezalek (Z. physik. Chem., 64, 727, 1908; etc.) assumed chemical combination between the components or association of one or both components. The work of Kendall on the solvation effect upon the solubility of solids provides the main support of this view. Cf. (Kendall, Davidson and Adler, J. A.C.S., 43, 1481, 1921).

On the physical side, van der Waals (Z. physik. Chem., 5, 133, 1890) considered that the deviations were due to the cohesive forces between the molecules, and van Laar (ibid., 72, 723, 1910; 83, 599, 1913) gave a slight modification. The main conclusion from the works of these authors is that the total vapour pressure of a solution should bear a linear relationship to the mol fraction only when the critical pressures of the components are the same. The van der Waal's theory gives the critical pressure

$$P_c = 8a/27b^2.$$

Since b is closely related to the molal volume, V, the critical pressure should bear a close relationship to the internal pressure, a/V^2.

The internal pressure theory, chiefly associated with Hildebrand (J.A.C.S., 38, 1452, 1916) arose from

the work of Rothmund (Z. physik. Chem., 26, 489, 1898) and Walden (ibid., 66, 409, 1909). Rothmund showed the general relationship between dielectric constant and solubility in some aqueous solutions. Walden pointed out the parallelism between dielectric constant and internal pressure, the qualitative rule being that, in water, the smaller the difference in internal pressure, the greater the mutual solubility of the two liquids. Since the solubility of a liquid in water seemed to be mainly governed by its polarity, Walden's conclusions are valid only for substances of low polarity, so that Rothmund's generalisation is probably the more correct in the case of water solutions. Hildebrand's conclusion is that, if the internal pressures of two liquids are the same, then in a solution each molecule may be under the same forces as in its pure liquid. The vapour pressure is determined merely by the proportion of the two molecules present, but deviations from Raoult's law may occur if the internal pressures are different. For systems in which the components are non polar, or approximately so, Hildebrand (J.A.C.S., 51, 66, 1929) proposed the equation

$$\bar{F}_2 - \bar{F}_2^{\circ} = RT \log N_2 - \alpha N_1^2 \qquad (6)$$

where $\bar{F}_2$ = molar free energy in the solution,

$\bar{F}_2^{\circ}$ = molar free energy in the pure liquid,

N_1 and N_2 = mol fractions of components,

and α a constant for a given mixture at a given temperature.

Hildebrand suggested a proportionality between the constant α and the difference in internal pressure of the two components, and solutions which satisfy the equation he terms "regular solutions", characterised by the absence of orienting and chemical effects. Since these intermolecular forces might be expected to be a function of the volume of the solution, and so of the spatial distribution of the molecules, Hildebrand and Wood (J. Chem. Physics, 1, 817, 1933) have derived the equation:-

$$F_2 - F_2^\circ = RT \log N_2 - A_{12} v_1, \qquad (7)$$

where $A_{12} = V_2 \left\{ \left(\frac{E_2}{V_2}\right)^{1/2} - \left(\frac{E_1}{V_1}\right)^{1/2} \right\}^2$

where v_1 = volume fraction of component 1,

E_1 and E_2 = the cohesive energies,

V_1 and V_2 = volumes per mol of the pure solvents.

Where the molecular structure of the components was known, excellent agreement has been found. When the molecular volumes are the same, equations (6) and (7) become identical. The constants α and A_{12} in these equations give a measure of the deviation of a system from ideal behaviour.

The close parallelism between the mutual solubility of liquids and their interfacial energy is the foundation of the "principle of independent surface

action", due to Langmuir (Coll. Symph. Mon., 3, 48, 1925). This is that the potential energy of a molecule in a liquid is composed additively of the interactions at the different parts of the interface between the molecule and its surroundings. Mathematically, if the molecules A and B have two kinds of surfaces, A and C, B and D, whose fractional areas are a and c, b and d respectively, then

$$\phi = ab\gamma_{ab} + ad\gamma_{ad} + bc\gamma_{bc} + cd\gamma_{cd} - ac\gamma_{ac} - bd\gamma_{bd}, \quad (8)$$

where ϕ = the "mixture energy",

γ_{ab} = interfacial energy for the surface between A and B, and so on. Langmuir's theory has been tested by Smyth and Engel (J.A.C.S., 51, 2646, 1929), by determining the partial vapour pressures of certain binary solutions. With non-polar solutions, they found a qualitative agreement, but, in other cases, considerable discrepances occurred, which they ascribed to the effect of dipoles. The work of Butler (Butler, Thomson and MacLennan, J.C.S., 674, 1933) on the partial vapour pressures of the lower normal aliphatic alcohols in water shows a general qualitative agreement with the theory.

In the general treatment of solubility, substances have been divided roughly into electrolytes and non-electrolytes, the former giving charged ions in aqueous

solution. In aqueous solutions, the long range forces between these ions is very important, but, in solvents of low dielectric constant, where free ions cannot exist, other forces of similar origin may be of importance. An electric field will be set up round a molecule when the individual charges of its component parts are unsymmetrically arranged, and the energy of transfer of such molecules, known as dipoles, quadrupoles, etc., according to their degree of complexity, to non-polar solvents has been calculated on certain assumptions. Martin (Phil. Mag., 8, 550, 1929), taking as his model two charged spheres in contact, obtained for the electrostatic energy of transfer of a dipole from a vacuum to a medium, dielectric constant D, the expression

$$F_e = \frac{\mu^2}{3a^3} \left\{ 1 - 1/D \right\}, \qquad (9)$$

where μ = dipole moment,

a = radius of the molecule.

Bell, (Trans. Far. Soc., 27, 797, 1931) using as model a rigid sphere where the distance between the electric centres forming the dipole is infinitely small in comparison with the radius of the sphere, derived the equation:-

$$F_e = \frac{\mu^2}{3a^3} \left\{ \frac{D - 1}{2D + 1} \right\} \qquad (10)$$

The relative solubilities of polar compounds in non-polar solvents should then be closely associated with the magnitude of the dipole moment and its radius,

yet but a few of the systems investigated have shown qualitative agreement.

Recently, London (Z. physik. Chem., 63, 245, 1930) has calculated the values of the "short range" van der Waals forces between two atoms, and has shown that these are due mainly to an interaction between short period electronic vibrations. In non polar solutions these forces are very important, but, with polar substances, the long range dipole forces cannot be ignored.

The interactions governing solubility may now be classified as:-

(1) the van der Waals, or dispersion, forces the approximate value of which between two atoms has been calculated by London,

(2) the interaction of dipoles with each other or with polarisable molecules,

(3) the interaction of ions with each other, with dipoles, or with polarisable molecules,

and (4) the interaction of two molecules involving compound formation by the mutual sharing of electrons.

The importance of each factor depends on the system under consideration.

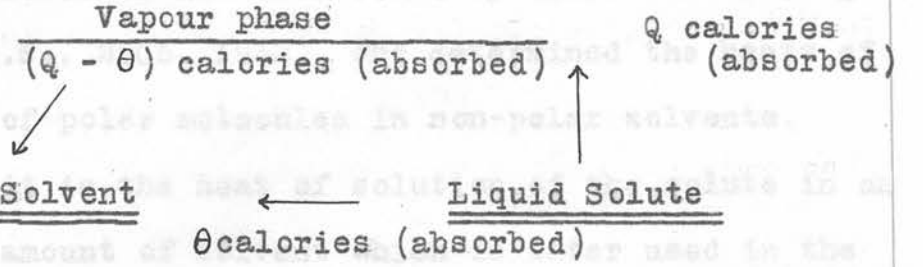
THERMODYNAMICAL THEORY.

A. The Heat of Solvation.

This thermodynamic function represents the heat absorbed in bringing the solute molecule from the vapour phase into an infinitely dilute solution, i.e. it is the heat of solution of the solute vapour. If Q is the heat of vaporisation of the pure liquid solute at a given temperature, θ its heat of solution in the solvent at infinite dilution, then the heat of solvation,

$$H = Q - \theta, \quad (11)$$

where heat absorbed is considered positive. Diagrammatically, the relation is



The heat of vaporisation, Q, can be calculated for any given temperature by means of the relation,

$$\frac{d(\log_e p)}{dT} = \frac{Q}{RT^2},$$

where p is the vapour pressure of the solute at absolute temperature T.

The values of Q at a given temperature T_0, given later, were calculated from the approximation,

$$\frac{\log_e p_2 - \log_e p_1}{T_2 - T_1} = \frac{Q}{RT_1T_2} \quad (12)$$

where p_2 and p_1 are the vapour pressures of the solute at temperatures T_2 and T_1, which were so chosen that $\frac{T_2 + T_1}{2} = T_0$. The average value of Q for a series of such temperatures was used. Q has been determined for a series of aliphatic alcohols (C_4 to C_8) at 25°C by Butler (Butler, Ramchandani and Thomson, J.C.S., 58, 1935) by vapour pressure measured, and these results are subsequently used.

Wolf (Wolf, Pahlke and Wehage, Z. physik. Chem., B 28, 1, 1935) found that the heat of solution, θ, approached a limiting value at infinite dilution, and the same relation has been found by other authors, eg. Bell (J.C.S., 2905, 1932), who determined the heats of solution of polar molecules in non-polar solvents.

And it is the heat of solution of the solute in an infinite amount of solvent which is later used in the determination of ΔH, the heat of solvation, the units being calories per mole of solute.

B. The Free Energy of Solvation.

The partial molar free energy of a solute in a binary solution at a given temperature may be expressed as

$$\bar{F}_2 = F_2^\circ + RT \log p_2/p_2^\circ \qquad (13)$$

where F_2° = molar free energy of the pure liquid solute,

p_2 = partial vapour pressure of solute,

p_2° = vapour pressure of pure solute.

In a solution which obeys Raoult's law,

$$p_2/p_2^\circ = N_2. \qquad (14)$$

When Raoult's law is not obeyed, we may write $p_2/p_2^\circ = N_2 f_2$, (15) where f_2 is an activity coefficient which measures the divergence from Raoult's law. As defined, $f_2 = 1$ in the pure liquid, i.e. when $N_2 \rightarrow 0$...

Substituting for p_2/p_2° in equation (13) the value $N_2 f_2$ (15), we have

$$\bar{F}_2 = F_2^\circ + RT \log N_2 f_2. \qquad (16)$$

Again, in an infinitely dilute solution, where the solute molecules are not associated, the partial molar free energy of the solute may be written as

$$\bar{F}_2 = \bar{F}_2^\circ + RT \log N_2 \qquad (17),$$

where $\bar{F}_2^\circ$ = standard molar free energy for the dilute solution.

If, in this dilute solution, f_2° is the activity coefficient, then, by combining equations (16) and (17), we obtain

$$\bar{F}_2^\circ - F_2^\circ = RT \log f_2^\circ \qquad (18)$$

Thus defined, the quantity RT log f_2° measures the difference between the molar free energy of the pure solute, F_2°, and its standard free energy in very dilute solutions, $\bar{F}_2^\circ$.

Butler (Butler, Thomson and MacLennan, J.C.S., 173, 1933) evaluated this quantity for a number of aliphatic

alcohols in water, at 25°C.

RT log $f_2°$, however, is not very susceptible to theoretical interpretation, and it is preferable to take as standard the gaseous state, since the above method involves a consideration of the substance as a pure liquid, which itself is a complex state.

However, $p_2/p_2°N_2$ and RT log $(p_2/p_2°N_2)$ have been evaluated for purposes of comparison in the following section.

Thus, if $F_{2g}°$ is the molar free energy of the solute in the vapour at unit pressure (1 mm. Hg) its free energy at a pressure p_2 is

$$\bar{F}_2 = F_{2g}° + RT \log p_2 \qquad (19)$$

so that, if p_2 is the partial pressure of the solute over a very dilute solution, molar fraction N_2, combining equations (17) and (19), we have

$$\bar{F}_2° + RT \log N_2 = \bar{F}_2 = F_{2g}° + RT \log p_2,$$

so that $$\bar{F}_2° - F_{2g}° = RT \log (p_2/N_2) \qquad (20)$$

and this quantity may be called the free energy of solvation which we may denote by ΔF_p.

The ratio (p_2/N_2), which is the limiting value, at small concentrations, of the distribution ratio of the solute between the vapour and the solvent, can be measured in two ways.

(a) By direct measurement of the partial vapour pressure, p_2, in a solution sufficiently dilute to pre-

vent interactions between solute molecules, or (b) when the miscibility is low, by the ratio $p_2°/N_s$, where $p_2°$ is the vapour pressure of the pure solute, N_s its molar fraction in the (dilute) saturated solution.

In case (a), assuming that Raoult's law holds for the solvent,

$$p_1 = p_1°N_1,$$ and if we measure

the relative molar concentrations, n_1 and n_2, of the solvent and solute in the vapour,

then $$n_2/n_1 = p_2/p_1°N_1, \qquad (21)$$

from which p_2 can be found.

By these methods Butler (Butler, Ramchandani and Thomson, loc. cit.) determined the free energy of solvation for the aliphatic alcohols (C_3 to c_8) in water, and of the lower normal aliphatic alcohols (C_1 to C_4), and other substances, in non polar solvents (Butler and Harrower, Trans. Farad. Soc., 33, 189, 1937).

Though p/N is very convenient in practice, a more natural expression of the distribution coefficient is the Ostwald coefficient λ,

where $$\lambda = c_\ell/c_g,$$

c_ℓ and c_g being the concentrations of the solute in the liquid and vapour in mols per cc. When the standard states are defined in terms of these units, the free energy change is

$$\Delta F_c = RT \log c_g/c_\ell$$

The relation between the two coefficients is

$$p/N = 1{\cdot}7032 \times 10^7 Td/273{\cdot}1\, M_1 \lambda ,$$

where M_1 = molecular weight of solvent,
and d = density of solvent at absolute temperature T,
so that

$$RT \log(p/N) = \Delta F_p = \Delta F_c + RT \log \left(\frac{1{\cdot}7032 \times 10^7 Td}{273{\cdot}1\, M_1} \right) \quad (22)$$

The free energy difference between the two scales of measurement can thus be found for any given temperature, T_0, and, by finding this difference for a series of temperatures, T_1 and T_2, such that $\frac{T_1 + T_2}{2} = T_0$, the corresponding entropy difference can be calculated, and thus the scale difference for the heat of solvation; so that the experimental results given later can be evaluated in terms of concentration units.

The entropy of solvation can be obtained in two ways;-

(a) We may use the relation

$$\frac{d(\Delta F)}{dT} = -\Delta S ,$$

where ΔS is the entropy of solvation at absolute temperature T, i.e. so defined, it is the temperature coefficient of the free energy. In practice, the approximation,

$$\frac{\Delta F_{T_2} - \Delta F_{T_1}}{T_2 - T_1} = -\Delta S_{T_0} \quad (23)$$

is convenient. The functions ΔF_{T_1}, ΔF_{T_2} are the

free energies at absolute temperatures T_1 and T_2, the entropy at temperature T_o, where $\frac{T_1 + T_2}{2} = T_o$.

Or, (b), the relation

$$\Delta F = \Delta H - T\Delta S \quad , \qquad (24)$$

may be employed when ΔH and ΔF are known for a given temperature T. Both methods have been used in the following experiments.

The above equation, (24), co-relates the thermodynamic functions, free energy, heat and entropy of solvation, and it is the purpose of these experiments to evaluate those quantities and discuss the relations between them.

E X P E R I M E N T A L

(I) Purification of Materials

(1) The alcohols used were B.D.H. products, and had previously been purified by Ramchandani in this Department.

As the only impurity seemed to be a trace of water, they were dried over fresh lime, refluxed and fractionated, the middle fractions being retained. The following boiling points were obtained;

Alcohol	B.P.	B.P./760 mms.
N-butyl alcohol	117·18 - 117·28/741·8	118·01
Sec-butyl alcohol	99·51 - 99·54/751·6	99·96
N-amyl alcohol	137·1 - 137·2 /747·4	137·75
Iso-amyl alcohol	131·15 - 131·35/761·2	131·33
Tert-amyl alcohol	101·42 - 101·48/744·2	102·11

(2) Glycerol

This was an A.R. product, containing 99·97 per

cent glycerol, and, being free from any objectionable impurity, and owing to its hygroscopic nature, it was considered unnecessary to purify it further. Its density was found to be D_4^{25} $1{\cdot}2552_1$.

(3) Acetone (B.D.H.)

As the only impurity in this product, distilled from the sodium iodide compound, seemed to be a trace of water, it was left for a few days over anhydrous copper sulphate then distilled and fractionated.
B.P. 55·89°C - 56·01°C/756·85mms.; 56·09/760 mms.

(4) Benzene (B.D.H.)

Extra pure benzene for molecular weight determinations, free from thiophene, was used. It was dried over lime which had been freshly burnt, fractionally distilled and then three times fractionally frozen.
B.P. 79·96°C - 80·04°C/761·6 mms.; 79·93°C/760 mms.

(5) Carbon Disulphide (B.D.H.)

This product was free from objectionable impurities, and was twice fractionated before use.
B.P. 46·35°C - 46·39°C/763·8 mms.; 46·20°C/760 mms.

(6) Chloroform

The MacFarlane and Co., (B.P.) product was used. This was shaken with concentrated sulphuric acid for 15 minutes to remove alcohol, washed with caustic soda solution and then with water. It was dried over anhydrous potassium carbonate and fractionated.

B.P. 60·75°C - 60·83°C/750·9 mms.; 61·21°C/760 mms.

(7) Diethyl Ether (MacFarlane and Co.)

This product was dried over sodium wire for a week, distilled, then fractionated three times.

B.P. 34·37°C - 34·41°C/755·5 mms.; 34·60°C/760 mms.

(8) Ethyl Acetate (B.D.H.)

Ethyl acetate was kept over anhydrous potassium carbonate to remove acid for 12 hours, then, to remove traces of water and alcohol, treated with phosphorus pentoxide. It was then fractionated, and the middle portion retained.

B.P. 76·71°C - 76·85°C/749·3 mms.; 77·24°C/760 mms.

II. Apparatus

After some preliminary work on very dilute solutions of the aliphatic alcohols in water, where the "three bulb" bubbler, previously employed by workers in this laboratory, was used, it was thought to improve the efficiency of the above apparatus by adding three more bulbs. This modification ensured complete saturation at the low concentrations used.

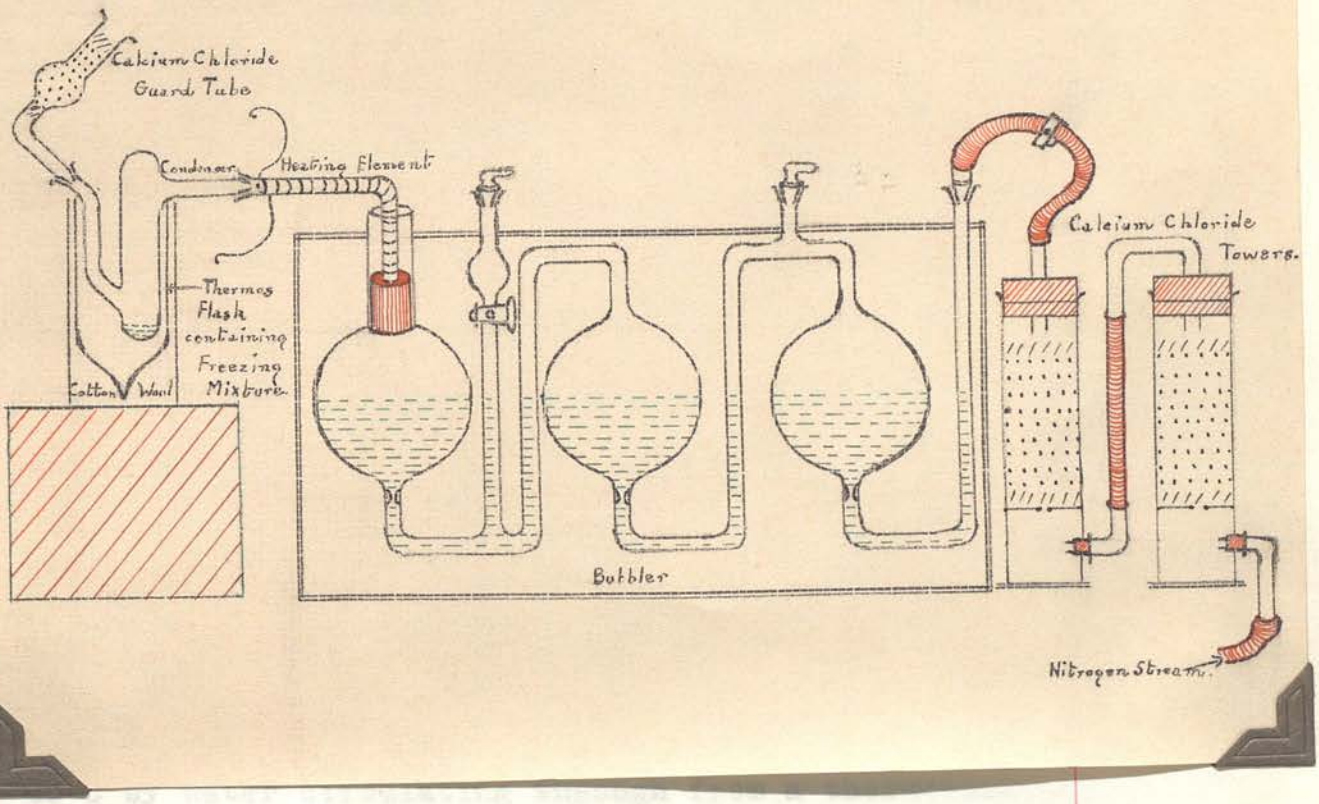
The Six-Bulb bubbler provided a vapour space large compared with that occupied by the standard solution, so that a greater surface than in the "Three-Bulb" type was exposed to the nitrogen stream, allowing of complete saturation in a short time.

It consisted of two sets of three bulbs, the larger set having bulbs of 250 ccs. capacity, the smaller of 50 ccs. The nitrogen passed through the larger bulbs first, where saturation was almost completed, and the smaller set ensured perfect saturation.

In each set, the bulbs were joined together as in Fig. II, with limbs fitted with ground glass joints. The two sets were connected by a ground glass joint arrangement, the whole being mounted on a wooden frame, weighted with lead. The constrictions on the entrance tubes broke the nitrogen stream into bubbles, which were allowed to pass at the rate of one bubble per second. A liquid trap was found to be unnecessary, as there was space sufficient to eliminate entrainment. The long limb, with stopcock and bulb, could be used to withdraw samples of the solution in order to ensure that the concentration had not appreciably altered.

To avoid premature condensation of the vapours, the exit tube was fitted with heating elements carried below the level of the thermostat water, from which they were protected by a short glass cylinder fitted with a one-holed rubber stopper. Heating mats on the horizontal portion of the exit tube were connected to these in series, and the electric current adjusted, by means of a resistance, to give a temperature slightly higher than the thermostat temperature.

Figure 2.


Calcium Chloride
Guard Tube
Condenser
Heating Element
Thermos
Flask
containing
Freezing
Mixture.
Cotton Wool
Bubbler
Calcium Chloride
Towers.
Nitrogen Stream.

Of the thermostats, that at 25°C was electrically heated, the other, at 35°C, gas heated. The temperatures were steady to ±0·01°C.

The vapours carried over by the nitrogen stream were liquefied or solidified by means of a condenser fitted on to the bubbler by a ground glass joint. The condenser was immersed in a slush of carbon dioxide snow and ether, contained in a thermos flask; atmosphere moisture was eliminated by attaching a calcium chloride tube to the condenser exit.

Analysis of Condensates

To determine the weight concentration of the condensate, a Rayleigh Interferometer was employed. This gave two series of vertical fringes in the eyepiece, the upper series being movable. In order to take a reading, a 1 cm. cell, fitted with a cover glass, was used. The reference solution, usually the pure solvent, was run into one cell compartment, the condensate into the other. The cover glass was firmly adjusted, and the cell put into a water-jacketed compartment, kept at 15°C by water circulating through from a thermostat.

Steady interferometer readings were quickly attained by this arrangement, speed being desirable in the case of organic solutions, where evaporation caused appreciable errors. Thus, in five minutes, a steady reading was obtained for water solutions, and organic

mixtures required ten minutes. The cell was so placed as to give a positive reading on matching the fringes, and the position of the condensate denoted R or L according as the condensate had to be run into the right or left compartment. The solution of higher refractive index appeared on the right. The zero reading was taken in each case by having the solvent in both compartments, and was always about 7 drum divisions below the zero mark on the scale, so that 7 drum divisions were added to each reading taken.

In the case of <u>water solutions</u>, the condensates were rarely homogeneous; so the collecting tube was weighed before and after the experiment, the difference giving the weight of condensate collected, w. From a burette, distilled water was then run into the condenser, 0·1 cc. at a time, the mixture being shaken after each addition till a homogeneous solution resulted. The weight was again found, and thus the weight of homogeneous solution, s. The concentration of this solution, c gms.%, was then found interferometrically, the weight percentage of solute in the original mixture being $\frac{s \times c}{w}$.

To find c, two accurate calibration solutions were prepared, with readings on either side of the condensate reading. About 50 drum divisions separated the calibration solution readings. The readings for condensate

and calibration solutions were taken one after the other to ensure that for each the same fringes had been matched. The approximate concentration of the condensate was first found by running known volumes of solute from a 1·0 cc. pipette into 10 ccs. water, and so calibrating over a wide range. The accurate calibrations could then be adjusted by volume, accurate weighings also being carried out during the various operations.

Over the short range (50 drum divisions) involved, the relation between refractive index and concentration may be assumed linear, so that the concentration, c, of the condensate could be read off from a large scale graph to 0·001%.

Or, if I_1, I_2 are the interferometer readings of the two calibration solutions, c_1, c_2 their concentrations, where $\begin{matrix} I_2 > I_1 \\ c_2 > c_1 \end{matrix}$ then a condensate of reading I has a concentration, $c = c_1 + \frac{I - I_1}{I_2 - I_1}(c_2 - c_1)$, where $I_2 > I > I_1$.

With <u>organic mixtures</u>, the condensates were invariably homogeneous, so the undiluted condensate reading was taken against the pure solvent as reference, or against a standard solution if the reading proved to be off the scale. As the fringes were more difficult to match than with water solutions, the refractive index - concentration curves were first found over a wide range.

Four 50 ml. standard flasks were used for this purpose. 10 ccs. of the solvent were run into each from a burette, and the weights determined. From a 0·5 cc. pipette, known volumes of solute were run into the flasks, which were weighed again. From the data, the weight concentrations were easily found, and graphed against the interferometer readings. The procedure was carried out with the pure solvents, but the error due to evaporation was negligible except with carbon disulphide, where the corrections were applied. The curves for the systems, ether-acetone and ethyl acetate-acetone were so insensitive that it was considered inadvisable to determine their partial vapour pressures.

Accurate calibration solutions were adjusted then by volume and by weight when the condensate reading had been determined. If these solutions did not conform to the wide range curves, the wrong fringe had been taken. In no case did this happen, but the method ensures accuracy where the graphs are not linear.

EXPERIMENTAL METHOD.

With water as solvent, standard solutions were prepared in a two-litre standard flask, with ground glass stopper.

A weighing bottle, fitted with a cork which was covered with tin foil, was half filled with the solute.

By means of a glass tube through the cork dipping below the liquid surface, a known weight of solute could be extracted and dropped into the standard flask containing a known mass of water.

In the case of organic solvents, evaporation caused appreciable errors. To avoid this, a ground glass joint, with a solid stopper, was sealed up and on the end was blown a bulb strong enough to contain the weight of liquid required. This could be hung on the balance by a hook on the stopper. The bulb was carefully cleaned, and, when the weight of solute added had been found, was dropped into a measured weight of solvent in a standard one-litre flask. The bulb broke, and the tube, on recovery, was again sealed up and blown out.

The bubblers were quickly filled with the solution, placed in the thermostats, (25°C and 35°C) and left for 15 minutes to attain the thermostat temperatures.

Meanwhile, the collecting tubes were thoroughly cleaned and dried, and calcium chloride tubes attached.

When the thermostats had regained their correct temperatures, nitrogen, dried by passing through calcium chloride towers, was passed through both bubblers simultaneously for ten minutes in order to saturate the solutions with the gas. This ensured that the same conditions held at the beginning and end of each experiment. The nitrogen was regulated by screw clips to one bubble per second.

Dry air was then sucked into the condensers through the calcium chloride guard tubes, and the condensers immersed in freezing mixtures of carbon dioxide snow and ether. Pads of cotton wool prevented heating of the freezing mixtures. The electric current was then switched through the heating elements.

As chloroform is attacked by oxygen and by light, additional precautions were taken when it was solvent. A sodium pyrogallate solution was placed between the nitrogen cylinder and the first calcium chloride tower to remove oxygen, and the bubbler in the electric thermostat covered with tin foil to exclude light from the heating lamp.

Any errors due to differences in construction of the bubblers were eliminated by interchanging them on the second running.

With water solutions, the experiments were run for 24 hours at least, 48 hours being necessary in the case of glycerol.

Organic solutions required about 8 hours in order to collect 0·5 cc. condensate.

On removal from the freezing mixtures, the condensates were allowed to regain atmospheric pressure and temperature by leaving the calcium chloride tubes attached for some time before finally stoppering them up. This ensured that no atmospheric moisture would subse-

quently be sucked into the condensers.

At least two concordant results were obtained in each case, the experimental error amounting to about 1% for organic solutions, and for water mixtures to about 0·5%.

This corresponds to an error of ±20 calories in the free energy, RT log p/N, for organic mixtures, and of ±10 calories with water as solvent. The error in the entropy is of the order ±0·2 for organic solvents, and ±0·1 calories per degree for water mixtures.

RESULTS

(a) Blank Experiments

Experiments were carried out with the pure solvents in the bubblers. The condensate readings were then taken against the pure solvents, and the error involved due to distillation of the solvent during an actual experiment thus found. The results are given in Table I.

The letters R and L mean that the condensate had to be placed in the right or left handed compartment of the interferometer cell in order to obtain a positive reading.

When an actual experiment was run, the position of the condensate was noted. Obviously, these distillation differences were subtracted from the condensate readings when the condensate collected from a mixture appeared in the same cell compartment, and added under the reverse conditions.

The solvents were distilled before use in each experiment in order that the corrections should universally apply.

TABLE I

Solvent		Condensate (25°C) I.R.	Condensate (25°C) Mean I.R.	Condensate (35°C) I.R.	Condensate (35°C) Mean I.R.
Acetone	L	1·0	1·5	2·0	2·0
		2·0		2·0	
Benzene	L	0·0	0·0	1·0	0·5
		0·5		0·5	
Carbon Disulphide	L	3·0	3·0	4·0	4·0
		2·5		4·0	
Chloroform	L	6·0	6·0	6·0	6·5
		6·0		7·0	
Diethyl Ether	L	2·0	2·0	-	-
		2·0		-	
Ethyl Acetate	L	8·5	8·0	-	-
		8·0		-	

Table II gives the vapour pressures of the pure solvents used. These were obtained from the International Critical Tables (Vol. III, p. 219).

TABLE II

Vapour Pressures.

Solvent	V.P. mms. (25°C)	V.P. mms. (35°C)
Water	23·77	42·19
Acetone	229·2	346·4
Benzene	94·41	147·7
Carbon Disulphide	358·9	515·0
Chloroform	199·1	301·3
Diethyl Ether	537·0	775·5
Ethyl Acetate	93·50	150·5

(b) The completed results for water as solvent and the organic solutes are given in Tables III to IX. N is the molar fraction of the solute in the solution, c its concentration (weight per cent.) and p its partial vapour pressure over the solution. The original calibration curves were drawn on a much wider scale so that 0·001 gms.% could be read off easily. The curves were assumed linear over the short range involved.

TABLE III (a)

Solvent Water	Calibration Solution		Diluted Condensate (25°C)		Initial Condensate (25°C)			
Solute	I.R.	Conc.%	I.R.	Conc.%	w gms.	s gms.	Conc.%	
Normal Butyl alcohol R	1766	6·236	1797	6·433	-	-	6·433	A
	1387	5·072	1802	6·452	-	-	6·452	
	1418	5·175						
	1827	6·537	1417	5·172	-	-	5·172	B
Sec BuOH R	1573	5·660	1586	5·712	-	-	5·712	
			1574	5·692	-	-	5·692	
	1601	5·772	1576	5·694	-	-	5·694	
Normal Amyl alcohol R	99	0·394	122	0·478	0·7159	6·585	4·395	A
	161	0·622	178	0·684	0·3206	2·048	4·368	
	201	0·767	171	0·660	0·1904	1·238	4·291	B
‡Iso AmOH L	1217	0·543	1218	0·544	0·2062	1·944	5·125	
	1243	0·555	1238	0·553	0·2193	2·028	5·109	
Tert AmOH R	970	3·272	989	3·337	0·2182	0·7515	11·49	
	1102	3·723	1701	5·236	0·3709	0·8123	11·47	
	1596	4·955						
	1774	5·431	1696	5·222	0·3831	0·8395	11·44	
Acetone L	1612	8·718	1621	8·764	1·0022	1·518	13·28	
	1723	9·283	1885	10·11	0·8188	1·064	13·13	
	1876	10·06						
	1980	10·59	1914	10·25	0·7241	0·9517	13·47	
Glycerol R	4·5	0·0401	5·4	0·0421	-	-	0·0421	
			4·5	0·0401	-	-	0·0401	
	6·3	0·0442	6·0	0·0435	-	-	0·0435	

‡ Zeiss Industrial Interferometer Used.

R Solution in Right-Hand Compartment of Cell.

L Solution in Left-Hand Compartment of Cell.

TABLE III (b)

Solvent Water	Calibration Solution		Diluted Condensate (35°C)		Initial Condensate (35°C)			
Solute	I.R.	Conc.%	I.R.	Conc.%	w gms.	s gms.	Conc.%	
Normal Butyl alcohol	1344	4·929	1362	4·989	0·7248	1·235	8·500	A
	1387	5·072	1851	6·617	0·8281	1·067	8·523	
	1827	6·537						
R	1896	6·766	1903	6·789	-	-	6·789	B
	1964	6·992	1903					
Sec BuOH	1952	7·122	1971	7·193	-	-	7·193	
			1969	7·188	-	-	7·188	
R	1991	7·270	1969	7·188	-	-	7·188	
Normal Amyl alcohol	161	0·622	161	0·622	0·7088	7·181	6·305	A
	201	0·767	194	0·741	0·4214	3·579	6·287	
R	284	1·069	256	0·967	0·5022	3·210	6·186	B
Tert AmOH	1217	0·543	1365	4·528	0·3215	1·051	14·79	
	1243	0·555	1770	5·420	0·6998	1·892	14·65	
R			1811	5·530	0·7107	1·876	14·59	
‡Iso AmOH	1301	4·324	1221	0·545	0·3381	4·387	7·073	
	1382	4·582						
L	1596	4·955	1224	0·546	0·3447	4·453	7·057	
	1770	5·431						
Acetone	1210	6·488	1342	7·506	0·9986	1·725	12·96	
	1351	7·575	1306	7·228	0·9075	1·631	12·99	
L			1289	7·097	0·8634	1·575	12·94	
Glycerol	26·1	0·0893	27·0	0·0913	-	-	0·0913	
	27·5	0·0925	26·8	0·0908	-	-	0·0908	
R			27·6	0·0927	-	-	0·0927	

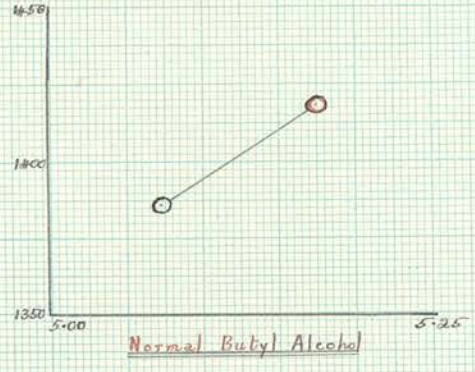
‡ Zeiss Industrial Interferometer Used.

Water Solvent

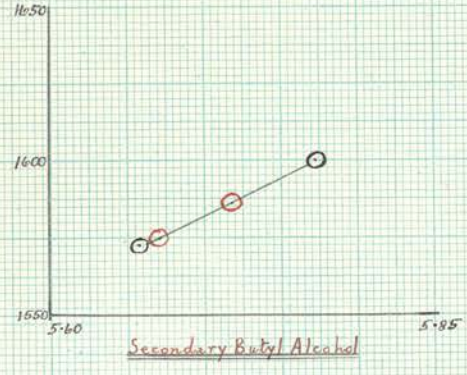
Calibration (25%) Curves

(1)

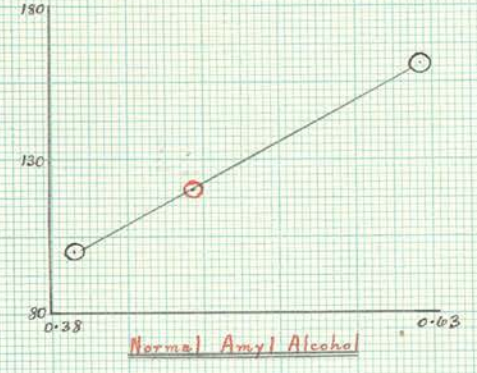
Normal Butyl Alcohol



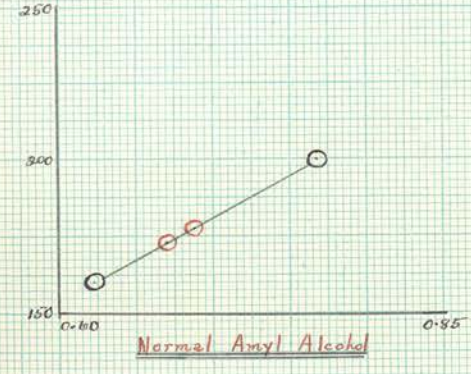
Normal Butyl Alcohol



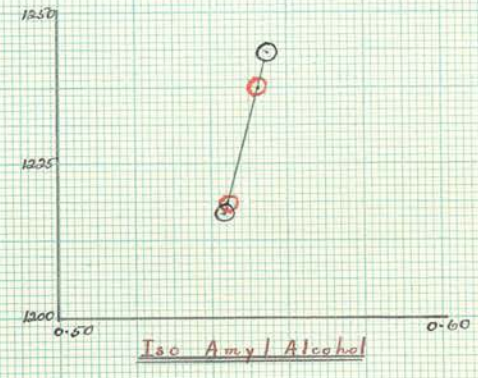
Secondary Butyl Alcohol



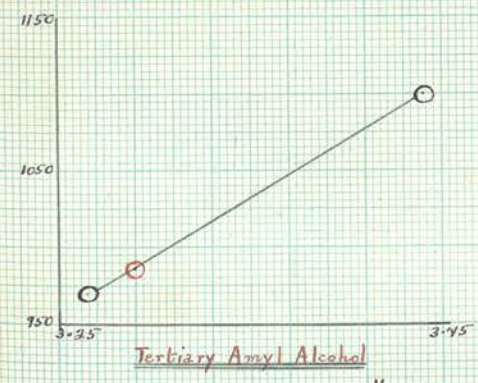
Normal Amyl Alcohol



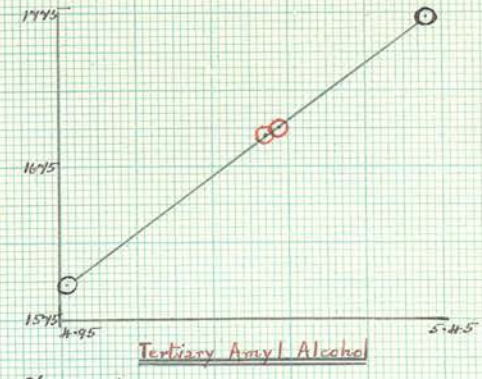
Normal Amyl Alcohol



Iso Amyl Alcohol



Tertiary Amyl Alcohol



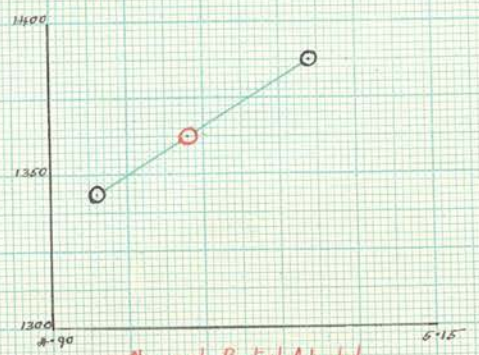
Tertiary Amyl Alcohol

Horiz. Concentration % Solute
Vert. Interferometer Reading
○ Condensate (Diluted)

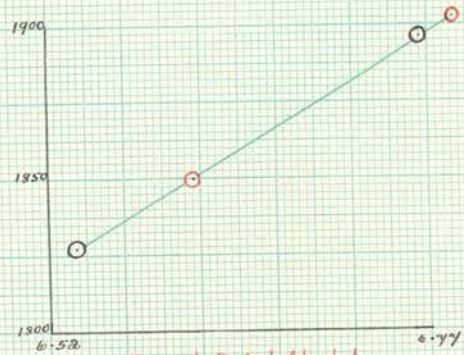
Water Solvent

Calibration 35% Curves

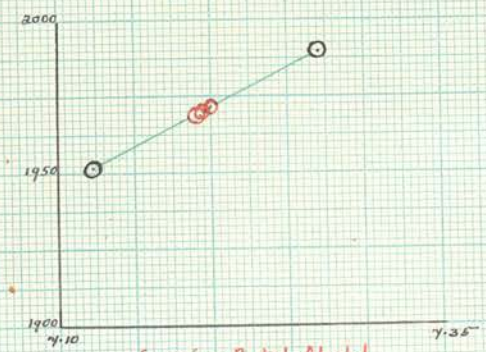
(2)



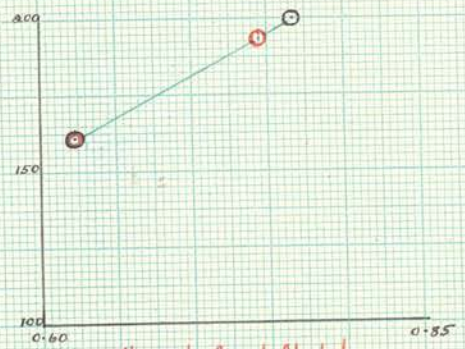
Normal Butyl Alcohol



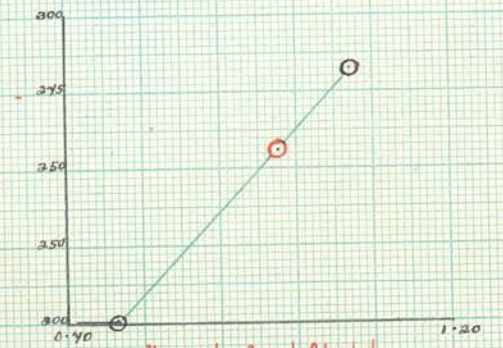
Normal Butyl Alcohol



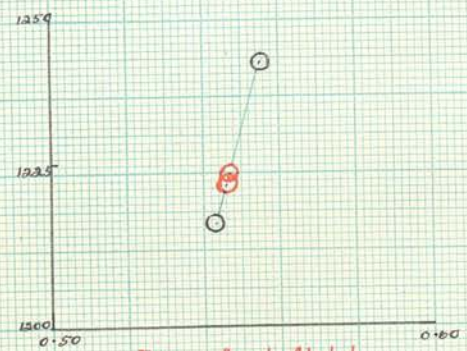
Secondary Butyl Alcohol



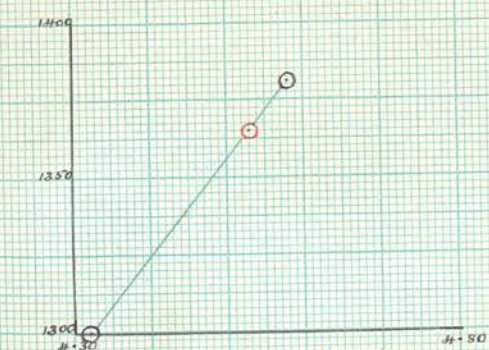
Normal Amyl Alcohol



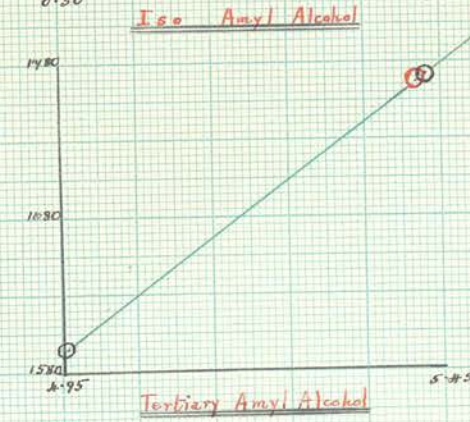
Normal Amyl Alcohol



Iso Amyl Alcohol



Tertiary Amyl Alcohol



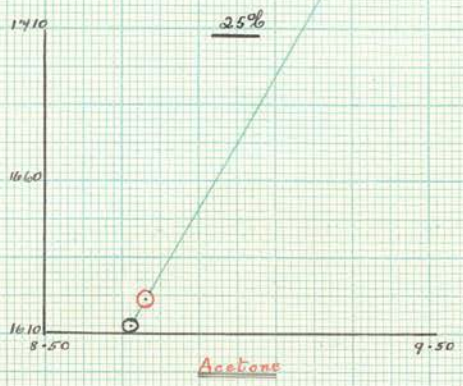
Tertiary Amyl Alcohol

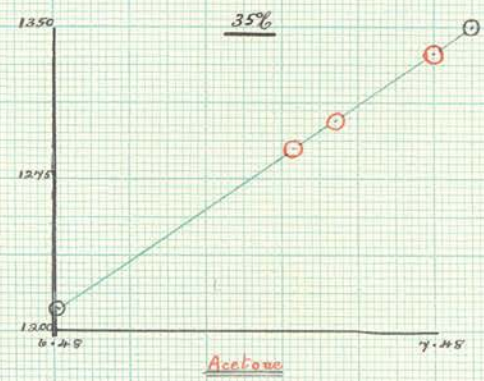
Horiz. Concentration % Solute
Vert. Interferometer Reading
○ Diluted Condensate Point

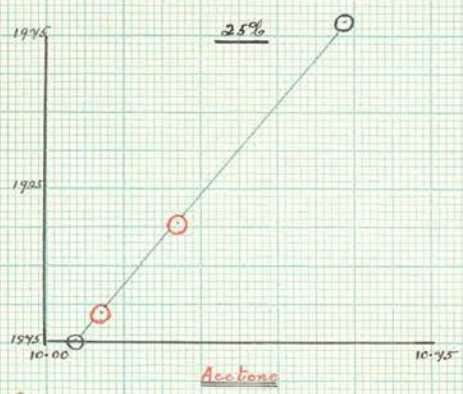
Water Solvent

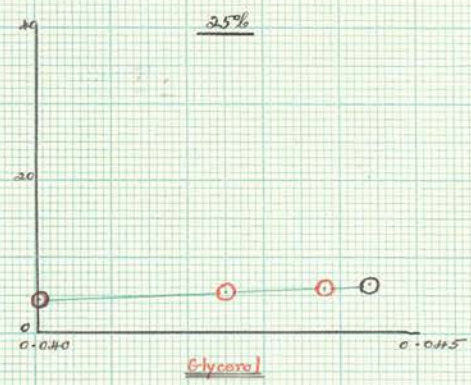
Calibration Curves

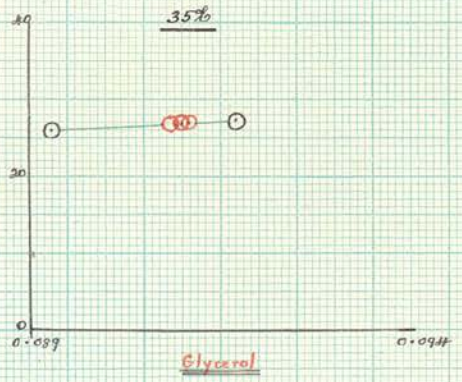
(3)











Horiz. Concentration % Solute

Vert. Interferometer Reading

○ Diluted Condensate Pt.

TABLE III (c)

Solvent Water.

Solute	$N \times 10^3$	Mean c%	p mms.	p/N	RT	log p/N cals.	Mean ΔS_{30}% cals./deg.
35°C	1·108	8·511	0·955	861·9		4144	
A 25°C	1·108	6·442	0·399	359·0		3490	
N-BuOH							65·2
35°C	0·863	6·789	0·747	866·2		4147	
B 25°C	0·863	5·172	0·315	365·6		3499	
35°C	0·821	7·189	0·795	968·5		4216	
Sec-BuOH 25°C	0·821	5·699	0·349	425·7		3590	62·6
35°C	0·413	6·296	0·580	1404		4442	
A 25°C	0·413	4·382	0·223	539·2		3731	
N-AmOH							71·2
35°C	0·397	6·186	0·569	1434		4456	
B 25°C	0·397	4·291	0·218	549·5		3742	
35°C	0·442	7·065	0·656	1485		4477	
Iso-AmOH 25°C	0·442	5·117	0·262	593·2		3787	69·0
35°C	1·087	14·68	1·484	1365		4427	
Tert-AmOH 25°C	1·087	11·47	0·630	578·8		3773	65·4
35°C	0·822	12·96	1·955	2378		4765	
Acetone 25°C	0·822	13·29	1·131	1376		4286	47·9
35°C	10·74	0·0916	0·0076	0·71		-213	
Glycerol 25°C	10·74	0·0419	0·0019	0·18		-1013	80·0

TABLE IV.

Solute Acetone (1) 35°C

(2) 25°C

Solvent	Preliminary Test Solutions		Calibration Solutions			Condensates		(1) 25°C (2) 35°C
	I.R.	Conc.%	I.R.		Conc%	Mean I.R.		Mean c%
Benzene	221	0·417	488	(1)	0·893	499	(1)	0·912
	495	0·905	534		0·976			
	822	1·700	488	(2)	0·893	523	(2)	0·956
L	1234	2·486	534		0·976			
CS_2	554	0·271	2048	(1)	1·219	2063	(1)	1·233
	1174	0·542	2083		1·251			
	1606	0·876	2142	(2)	1·290	2148	(2)	1·298
L	2150	1·301	2150		1·301			
Chloroform	231	0·558	100	(1)	0·278	117	(1)	0·324
	448	1·069	116		0·321			
	827	2·092	100	(2)	0·278	105	(2)	0·291
L	1015	2·542	116		0·321			

Table IV (Contd.)

Solvent	$N \times 10^2$ Mean c%	p mms.	p/N	RT log p/N cals.	ΔS_{30}/cals./deg.
35°C	0·912	1·828	347·1	3586	
Benzene 0·527					35·4
25°C	0·956	1·226	232·8	3232	
35°C	1·233	8·416	1214	4354	
CS_2 0·693					32·6
25°C	1·298	6·181	892·1	4028	
35°C	0·324	2·013	151·0	3076	
Chloroform 1·334					40·9
25°C	0·291	1·196	89·73	2667	

TABLE V.

Solute Benzene.

Solvent	Preliminary Test Solutions		Calibration Solutions			Condensates (1) 35°C (2) 25°C		
	I.R.	Conc.%	I.R.		Conc.%	Mean I.R.		Mean c%
Acetone	207	0·562	295	(1)	0·808	301	(1)	0·828
	444	1·223	323		0·908			
	823	2·251	295		0·808	293	(2)	0·815
R	1618	4·294	323	(2)	0·908			
CS_2	279	0·315	359		0·408	384	(1)	0·452
	612	0·701	384	(1)	0·452			
	871	0·981	359		0·408	373	(2)	0·433
L	1365	1·748	384	(2)	0·452			
Chloroform	198	0·640	52		0·187	88	(1)	0·316
	374	1·224	93	(1)	0·336			
	453	1·773	52		0·187	83	(2)	0·300
R	707	2·330	93	(2)	0·336			
Ethyl Acetate	193	0·525						
	376	1·008	332		0·900	353	(2)	0·955
	746	1·992	358	(2)	0·968			
R	1026	2·857						

TABLE V (Contd.)

Solvent	$N \times 10^2$	Mean c%	p mms.	p/N	RT	log p/N cals.	ΔS_{30} cals./deg.
35°C	1·033	0·828	2·150	208·2		3273	
Acetone	1·033						36·1
25°C		0·815	1·401	135·6		2912	
35°C		0·452	2·276	246·5		3377	
CS_2	0·923						35·1
25°C		0·433	1·518	164·4		3026	
35°C		0·316	1·461	141·5		3036	
Chloroform	1·033						37·6
25°C		0·300	0·915	88·59		2660	
Ethyl Acetate 25°C	1·033	0·955	1·016	98·33		2721	-

TABLE VI.

Solute Carbon Disulphide.

Solvent	Preliminary Test Solutions		Calibration Solutions			Condensates		(1) 35°C (2) 25°C
	I.R.	Conc.%	I.R.		Conc.%	Mean I.R.		Mean c%
Acetone	423	0·855	1454	(1)	3·211	1490	(1)	3·292
	1075	2·396	1494		3·301			
	1494	3·301	1682	(2)	3·700	1723	(2)	3·785
R	1746	3·835	1728		3·795			
Benzene	365	1·479	840	(1)	3·287	869	(1)	3·402
	729	2·849	885		3·465			
	920	3·589	944	(2)	3·682	979	(2)	3·824
R	1419	5·441	991		3·873			
Chloroform	221	0·491	875	(1)	1·471	882	(1)	1·483
	511	0·881	916		1·542			
	1017	1·695	916	(2)	1·542	957	(2)	1·608
R	1538	2·551	968		1·626			

TABLE VI (Contd.)

Solvent	$N \times 10^2$	Mean c%	p mms.	p/N	RT log p/N cals.	ΔS_{30} cals./deg.
35°C		3·292	9·010	1690	4557	
Acetone	0·533					30·8
25°C		3·785	6·889	1293	4249	
35°C		3·402	5·343	766·5	4072	
Benzene	0·697					32·6
25°C		3·824	3·856	553·1	3746	
35°C		1·483	7·125	704·4	4020	
Chloroform	1·012					32·8
25°C		1·608	5·111	505·2	3692	

TABLE VII.

Solute Chloroform.

Solvent	Preliminary Test Solutions		Calibration Solutions		Condensates		(1) 35°C (2) 25°C
	I.R.	Conc.%	I.R.	Conc.%	Mean I.R.		Mean c%
Acetone	116	0·939	(1)		142	(1)	1·144
	234	1·879	125	1·007			
	325	2·815	143	1·152			
R	1040	8·294	(2)		133	(2)	1·071
Benzene	218	0·831			420	(1)	2·328
	343	1·683	386	2·050			
	431	2·426	424	2·365			
L	458	3·321			423	(2)	2·357
CS_2	415	0·608			809	(1)	1·163
	840	1·207	782	1·125			
	1162	1·731	821	1·181			
L	1480	2·264			788	(2)	1·134
Diethyl Ether	159	1·077	21	0·175	26	(2)	0·210
	783	5·121	(2)				
			39	0·300			
R	1055	6·834					
Ethyl Acetate	188	1·667					
	369	3·227	162	1·441	171	(2)	1·518
	547	4·866	199	1·759			
R	731	6·342					

TABLE VII.(Contd.)

Solvent		$N \times 10^2$	Mean c%	p mms.	p/N	RT	log p/N	$\Delta S_{30°C}$
	35°C		1·144	1·948	208·3	3274		
Acetone		0·935						39·2
	25°C		1·071	1·206	129·0	2882		
	35°C		2·328	2·302	253·8	3394		
Benzene		0·907						36·8
	25°C		2·357	1·490	164·3	3026		
	35°C		1·163	3·857	425·0	3710		
CS_2		0·907						35·0
	25°C		1·134	2·620	288·7	3360		
Ether	25°C	0·903	0·210	0·701	77·67	2581		-
Ethyl Acetate	25°C	0·941	1·518	1·063	112·9	2803		-

TABLE VIII.

Solute Diethyl Ether (25°C).

Solvent	Preliminary Test Solutions		Calibration Solutions		Condensate (25°C)	
	I.R.	Conc.%	I.R.	Conc.%	Mean I.R.	Mean c%
	192	0·363				
	439	0·749				
Benzene	877	1·624	604	1·061	604	1·061
	1254	2·369				
L	1490	2·671				
	327	1·101				
			2000	1·141		
CS_2	392	0·157			2059	1·195
			2065	1·200		
L	2065	1·200				
	176	0·421				
	400	0·956				
Chloroform			247	0·593		
	798	1·932			255	0·613
			263	0·632		
L	969	2·187				

Solvent	$N \times 10^2$	Mean c%	p mms.	p/N	RT log p/N	$\Delta S_{30°C.}$
Benzene 25°C	0·702	1·061	1·067	151·9	2979	-
CS_2 25°C	0·431	1·195	4·453	1033	4117	-
Chloroform 25°C	1·131	0·613	1·979	175·1	3063	-

TABLE IX.

Solute Ethyl Acetate.

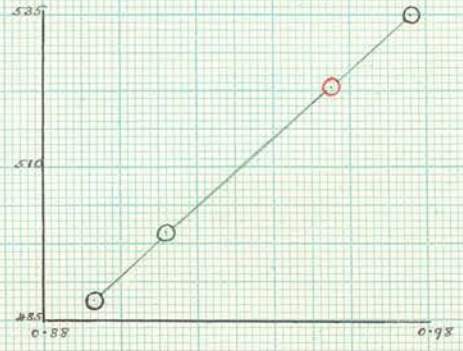
	Preliminary Test Solutions		Calibration Solutions		Condensates (1) 35°C (2) 25°C		
Solvent	I.R.	Conc.%	I.R.	Conc.%	Mean I.R.		Mean c%
	218	0·557		(1)	501	(1)	1·242
	281	0·699	484	1·195			
Benzene	431	1·061	530	1·323			
L	827	2·034		(2)	495	(2)	1·226
	468	0·332			541	(1)	0·386
	983	0·685	516	0·365			
CS_2	1048	0·734	545	0·390			
L	1522	1·059			528	(2) 0·375	
	401	1·210			69	(1) 0·198	
			59	0·159			
Chloroform	545	1·783					
			97	0·305			
L	765	2·275			66	(2) 0·167	

Solvent	$N \times 10^2$	Mean c%	p mms.	p/N	RT log p/N	$\Delta S_{30°C.}$
		1·242	1·645	159·4	3109	
Benzene	1·033					37·5
		1·226	1·039	100·6	2734	
		0·386	1·722	340·0	3573	
CS_2	0·507					34·8
		0·375	1·164	230·2	3225	
		0·198	0·811	71·66	2619	
Chloroform	1·132					43·3
		0·167	0·452	39·91	2186	

Organic Solvents

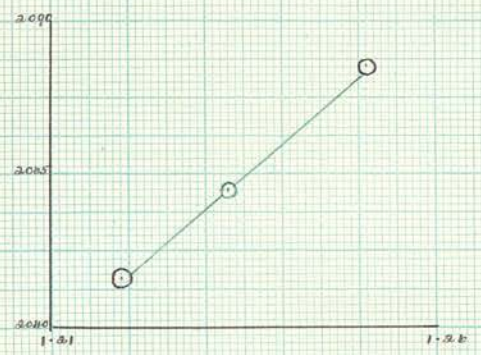
Calibration Curves

(1)

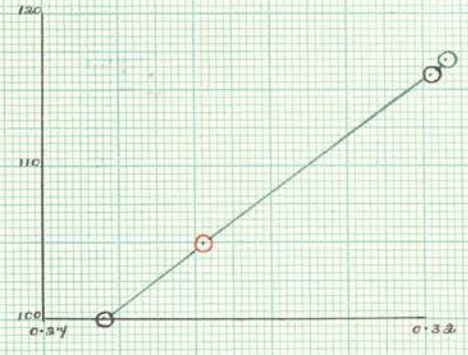


Solute → Acetone in Benzene ← Solvent Solute →

Acetone in Carbon Disulphide ← Solvent

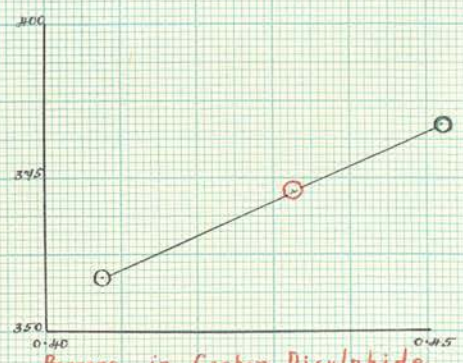


Solute → Acetone in Carbon Disulphide ← Solvent Solute →



Acetone in Chloroform ← Solvent

Solute → Benzene in Acetone ← Solvent Solute →



Benzene in Carbon Disulphide ← Solvent

Horiz. Concentration % Solute

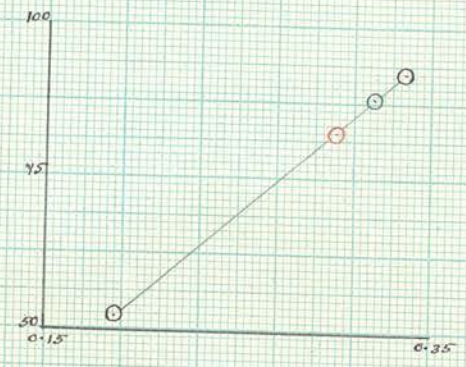
Vert. Interferometer Reading

○ 25% ○ 35% Mean Condensate Positions

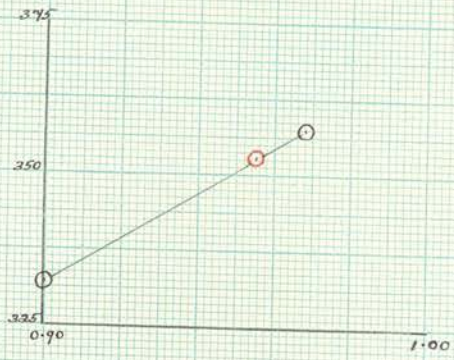
Organic Solvents

Calibration Curves

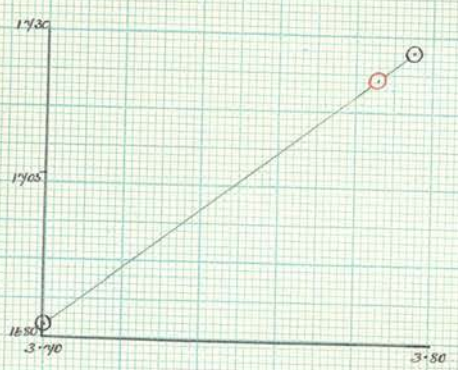
(2)



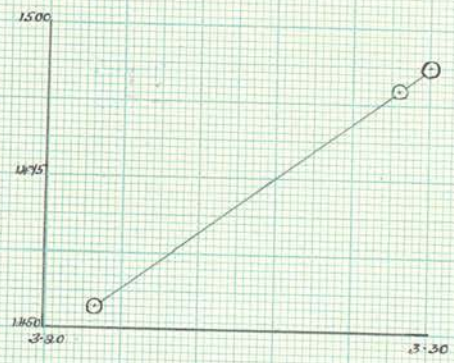
Benzene in Chloroform.



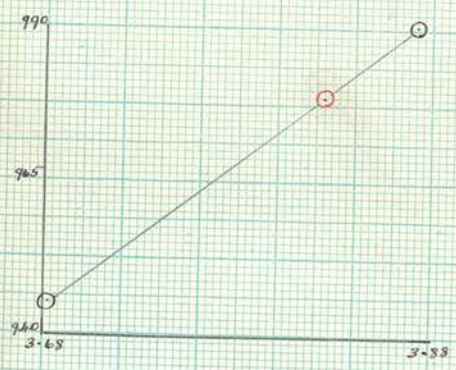
Benzene in Ethyl Acetate.



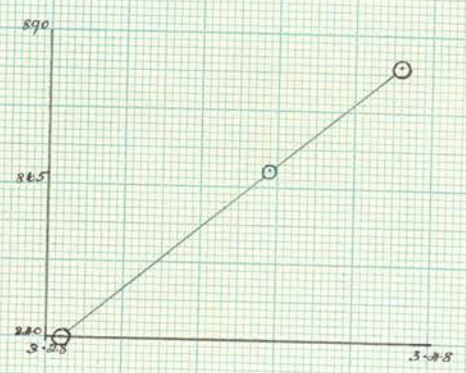
Carbon Disulphide in Acetone



Carbon Disulphide in Acetone



Carbon Disulphide in Benzene



Carbon Disulphide in Benzene

Horiz. Concentration % Solute

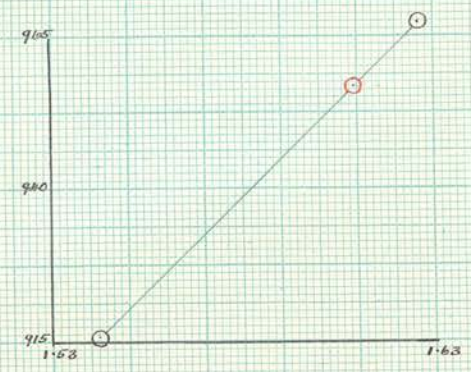
Vert. Interferometer Reading

○ 25% Mean Condensate Positions
○ 35%

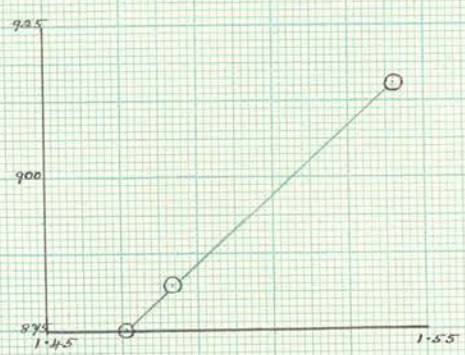
Organic Solvents

Calibration Curves

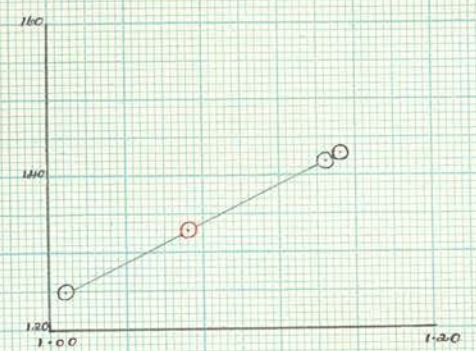
(3)



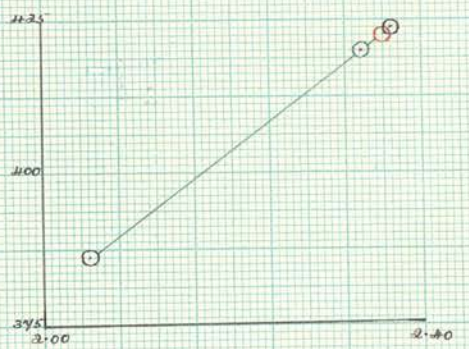
Carbon Disulphide in Chloroform



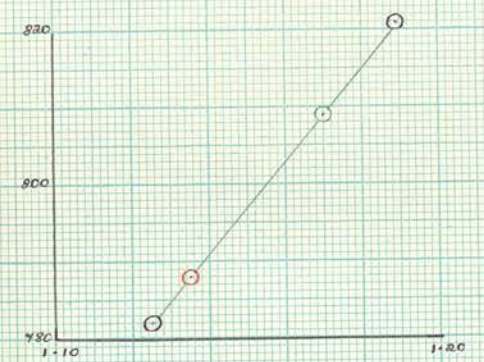
Carbon Disulphide in Chloroform



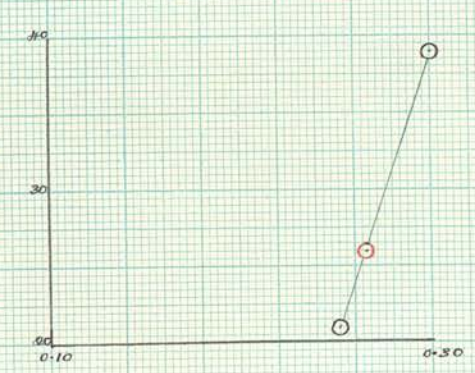
Chloroform in Acetone



Chloroform in Benzene



Chloroform in Carbon Disulphide



Chloroform in Diethyl Ether

Horiz. Concentration % Solute

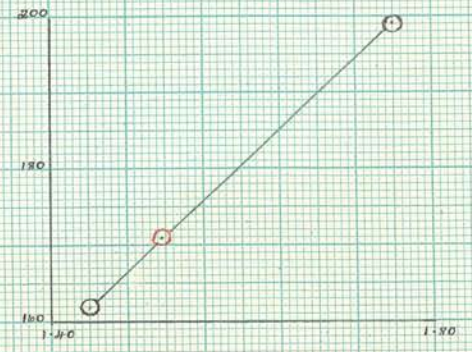
Vert. Interferometer Reading

○ 25% ○ 35% Mean Condensate Positions

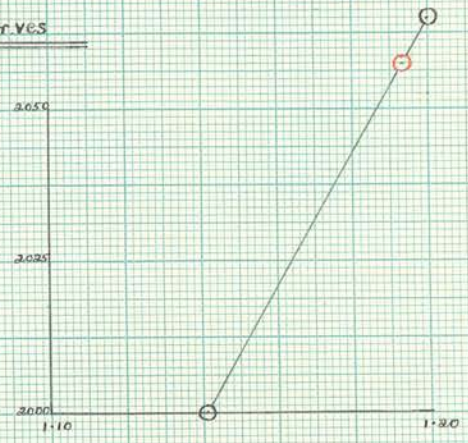
Organic Solvents

Calibration Curves

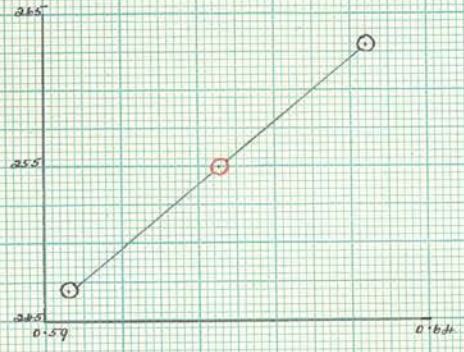
(H)



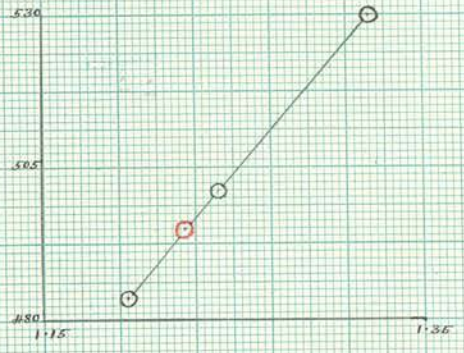
Chloroform in Ethyl Acetate



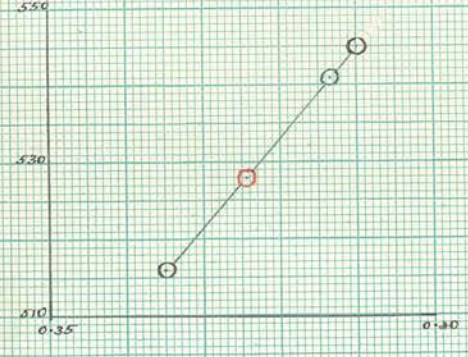
Diethyl Ether in Carbon Disulphide



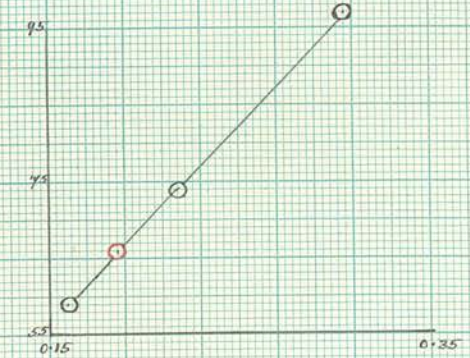
Diethyl Ether in Chloroform



Ethyl Acetate in Benzene



Ethyl Acetate in Carbon Disulphide



Ethyl Acetate in Chloroform

Horiz. Concentration % Solute

Vert. Interferometer Reading

○ 25%
○ 35% Mean Condensates Positions

In the foregoing results, the quantity p/N represents the distribution ratio of the solute between the vapour and the solution.

Though (p/N) is convenient in practice, the distribution coefficient is more naturally expressed in terms of the Ostwald coefficient,

$$\lambda = c_\ell / c_g$$

where c_ℓ, c_g are the concentrations of the solute in the liquid and vapour in mols./cc.

The free energy of solvation in terms of these units is then $\Delta F_c = RT \log c_g/c_\ell = -RT \log \lambda$

The relation between these expressions at absolute temperature T is

$$p/N = (1{\cdot}7032 \times 10^7) T . d_1 / 273{\cdot}1 M_1 \lambda$$

where M_1 is the molecular weight of the solvent, d_1 its density. So that

$$\Delta F_p - \Delta F_c = RT \log \left(\frac{1{\cdot}7032 \times 10^7 \times T \times d_1}{273{\cdot}1 \times M_1} \right)$$

By finding this scale difference at 20°C and 30°C, we thus find the corresponding entropy difference at 25°C, from the relation $\frac{d(\Delta F)}{dT} = -\Delta S$; for, over a small range of temperature, (10°C) this becomes

$$\frac{\Delta F_{30°} - \Delta F_{20°}}{303{\cdot}1 - 293{\cdot}1} = -\Delta S_{25°}$$

i.e. $$\frac{\Delta F_{30} - \Delta F_{20}}{10} = -\Delta S_{25°}.$$

Then, knowing $\Delta F_p - \Delta F_c$

and $\Delta S_c - \Delta S_p$,

we can find the difference, $(\Delta H_c - \Delta H_p)$, from the equation $\Delta F = \Delta H - T\Delta S$.

These differences have been calculated in the following table and applied to the experimental results which have thus been reduced to the concentration scale. The densities in Table Xa were obtained from the I.C.T. (Vol III p. 110.)

TABLE X (a)

Solvent	Density (20°C)	Density (25°C)	Density (30°C)
Water	0·9982	0·9971	0·9957
Diethyl ether	0·7135	0·7077	0·7018
Chloroform	1·4891	1·4797	1·4700
Acetone	0·7901	0·7844	0·7787
Benzene	0·8788	0·8734	0·8681
CS_2	1·2630	1·2554	1·2480
Ethyl acetate	0·9014	0·8941	0·8877

TABLE X (b)

Solvent	$(\Delta F_p-\Delta F_c)_{20°}$	$(\Delta F_p-\Delta F_c)_{25°}$	$(\Delta F_p-\Delta F_c)_{30°}$	$(\Delta S_c-\Delta S_p)_{25°}$
Water	8,063	8,210	8,357	29·4
Ether	7,043	7,166	7,293	25·0
$CHCl_3$	7,194	7,323	7,452	25·8
Acetone	7,245	7,374	7,503	25·8
Benzene	7,133	7,261	7,389	25·6
CS_2	7,362	7,494	7,626	26·4
Ethyl acetate	7,078	7,204	7,330	25·2

TABLE X (c)

Solvent	$(\Delta F_p-\Delta F_c)_{25°}$	$(\Delta S_c-\Delta S_p)_{25°}$	$T(\Delta S_c-\Delta S_p)_{25°}$	$(\Delta H_c-\Delta H_p)_{25°}$
Water	8,210	29·4	8,762	552
Ether	7,166	25·0	7,450	284
$CHCl_3$	7,323	25·8	7,690	367
Acetone	7,374	25·8	7,690	316
Benzene	7,261	25·6	7,630	369
CS_2	7,494	26·4	7,868	374
Ethyl acetate	7,204	25·2	7,511	307

For the pure solute, the molar fraction N, becomes unity, so that RT log p/N becomes RT log p°, where p° is the vapour pressure of the liquid at temperature T.

ΔH, for the pure solute becomes Q, the heat of vaporisation, since the heat of solution, θ is zero.

Q was calculated from the relation

$$\frac{d \log p}{dT} = \frac{Q}{RT^2}, \text{ by using the approximation}$$

$$\frac{\log p_2 - \log p_1}{T_2 - T_1} = \frac{Q}{RT_1T_2}.$$

Temperatures T_1 and T_2 were so chosen that $T_1 + T_2/2 = 298{\cdot}1°K$, and the average Q found for a series of such temperatures.

Then $$\Delta S^{\circ}_{25°} = \frac{\Delta H^{\circ}_{25°} - \Delta F^{\circ}_{25°}}{298{\cdot}1}.$$

Table XI gives these quantities for the pure substances, and ΔF°_c, ΔH°_c, ΔS°_c have been found by conversion of scales given in Table X.

TABLE XI (a)

Substance	Molecular Weight (gms.)	$p^\circ_{25°C.}$	$p^\circ_{35°C.}$
Acetone	58·05	229·2	346·4
Benzene	78·05	94·41	147·7
CS_2	76·00	358·9	515·0
Chloroform	119·4	199·1	301·3
Diethyl Ether	74·08	537·0	775·5
Ethyl Acetate	88·06	93·50	150·5

TABLE XI (b) 25°C

Substance	RT log p° (ΔF°_μ)	$-\Delta H^\circ_p$ cals.	$-T\Delta S^\circ_p$ cals.	$-\Delta S^\circ_p$ cals/deg.
Acetone	3,220	7,580	10,800	36·2
Benzene	2,695	8,180	10,875	36·5
CS_2	3,490	6,620	10,110	33·9
Chloroform	3,140	7,640	10,780	36·2
Diethyl Ether	3,730	6,750	10,480	35·2
Ethyl Acetate	2,690	8,640	11,330	38·0

TABLE XI (c) 25°C

Substance	$-\Delta F^\circ_c$	$-\Delta H^\circ_c$	$-T\Delta S^\circ_c$	$-\Delta S^\circ_c$
Acetone	4155	7,265	3,110	10·4
Benzene	4565	7,810	3,245	10·9
CS_2	4005	6,245	2,240	7·5
Chloroform	4185	7,275	3,090	10·4
Diethyl Ether	3435	6,465	3,030	10·2
Ethyl Acetate	4515	8,335	3,820	12·8

If Raoult's Law holds, $p/p^{\circ}N$ is unity, and the deviations from the law are positive or negative according as $p/p^{\circ}N$ is greater or less than unity. Thus RT log $p/p^{\circ}N$, which is really the free energy referred to the liquid as standard, is positive or negative according as the deviation is positive or negative.

ΔH_p can be calculated from the equation $\Delta H_p = Q - \theta$, where Q is the heat of vaporisation of the pure liquid solute at a given temperature T, and θ is the heat of solution of the pure liquid solute in the pure liquid solvent, heat absorbed being considered positive; so that ΔH_p represents the heat of solution of the solute vapour in the liquid solvent. In the following Tables (XII -XVIII) ΔF, ΔH, and ΔS, have been found in terms of concentrations units also, by using Table XI (c).

TABLE XII (a)

Solvent Water (25°C)

Solute	p°	p/N	p/p°N	RT log p°	RT log p/N	RT log p/p°N
MeOH	122·2	184	1·51	2,850	3,090	244
EtOH	59·0	218	3·69	2,418	3,190	774
n-PrOH	20·1	291	14·40	1,779	3,380	1,582
iso-PrOH	44·0	339	7·70	2,245	3,450	1,211
n-BuOH	6·8	363·3	52·9	1,137	3,495	2,353
iso-BuOH	11·6	499	43·2	1,454	3,680	2,234
sec-BuOH	17·2	425·7	25·1	1,687	3,590	1,912
tert-BuOH	42·4	503	11·8	2,222	3,690	1,464
n-AmOH	2·5	544·4	214	543	3,736	3,182
iso-AmOH	3·1	593·2	191	671	3,787	3,115
tert-AmOH	16·7	578·8	35	1,670	3,773	2,108
Acetone	229·2	1376	6·0	3,222	4,286	1,063

TABLE XII (b)

Solute	Q cals.	$-\theta_\infty$ cals.	$-\Delta H_p$ (Observed)
MeOH	9,240	2,000	11,240
EtOH	12,330	2,550	12,880
n-PrOH	11,370	3,050	14,420
iso-PrOH	9,680	3,770	13,450
iso-BuOH	12,340	2,900	15,240
tert-BuOH	11,200	3,240	14,440
Acetone	7,580	2,510	10,090

In the above tables, the results are combined with those of Ramchandani and Thomson (Butler, Ramchandani and Thomson, J.C.S., 58, 1935). Q and θ_∞ were calculated from the I.C.T. figures (Vol. III).

TABLE XII (c) Solvent Water (25°C)

Solute	ΔF_p	$-\Delta S_p$	$-T\Delta S_p$	$-\Delta H_p$
MeOH	3,090	48·2	14,330	11,240
EtOH	3,190	54·0	16,070	12,880
n-PrOH	3,380	59·7	17,800	14,420
iso-PrOH	3,450	56·7	16,900	13,450
n-BuOH	3,495	65·2	19,435	15,940 (Calc)
iso-BuOH	3,680	63·6	18,920	15,240
sec-BuOH	3,590	62·6	18,650	15,060
tert-BuOH	3,690	60·8	18,130	14,440
n-AmOH	3,736	71·2	21,240	17,500
iso-AmOH	3,787	69·0	20,560	16,770
tert-AmOH	3,773	65·4	19,490	15,720
Acetone	4,286	47·9	14,280	9,990

TABLE XII (d)

Solute	ΔF_c	$-\Delta S_c$	$-T\Delta S_c$	$-\Delta H_c$
MeOH	5,120	18·8	5,570	10,690
EtOH	5,020	24·6	7,310	12,330
n-PrOH	4,830	30·3	9,040	13,870
iso-PrOH	4,760	27·3	8,140	12,900
n-BuOH	4,715	35·8	10,675	15,390
iso-BuOH	4,530	34·2	10,160	14,690
sec-BuOH	4,620	33·2	9,890	14,510
tert-BuOH	4,520	31·4	9,370	13,890
n-AmOH	4,470	41·8	12,480	16,950
iso-AmOH	4,429	39·6	11,800	16,220
tert-AmOH	4,440	36·0	10,730	15,170
Acetone	3,920	18·5	5,520	9,440

TABLE XIII (a)

Solute Acetone.

Solvent	p/N 25°C	p/p°N 25°C	RT log p/p°N 25°C	p/N 35°C	p/p°N 35°C
Benzene	232·8	1·016	+9·3	347·1	1·002
CS_2	892·1	3·892	+806·0	1,214	3·506
Chloroform	89·73	0·392	-556·2	151·0	0·436
Acetone	229·2	1·000	±0	346·4	1·000

TABLE XIII(b)

25°C

Solvent	Q cals. (ΔH°)	- θ_∞ cals.	$-\Delta H_p$ cals.
Benzene	-	-310	-7,270
CS_2	-	-1,795	5,785
Chloroform	-	+1,915	9,495
Acetone	7,580	±0	7,580

TABLE XIII (c)

25°C

Solvent	ΔF_p	$-\Delta H_p$	$-T\Delta S_p$	$-\Delta S_p$
Benzene	3,230	7,270	10,500	35·2
CS_2	4,030	5,785	9,815	32·9
Chloroform	2,665	9,495	12,160	40·8
Acetone	3,220	7,580	10,800	36·2

TABLE XIII (d)

25°C

Solvent	$-\Delta F_c$	$-\Delta H_c$	$-T\Delta S_c$	$-\Delta S_c$
Benzene	4,030	6,900	2,870	9·6
CS_2	3,465	5,410	1,945	6·5
Chloroform	4,655	9,130	4,475	15·0
Acetone	4,155	7,265	3,100	10·4

TABLE XIV (a)

Solute Benzene.

Solvent	p/N 25°C	p/p°N 25°C	RT log p/p°N 25°C	p/N 35°C	p/p°N 35°C
Acetone	135·6	1·436	+214·7	208·2	1·409
CS_2	164·4	1·742	+329·1	246·5	1·669
Chloroform	88·59	0·938	-37·8	141·5	0·957
Ethyl Acetate	98·33	1·042	+24·2	-	1·033 (Calc.)
Ben zene	94·41	1·000	±0	147·7	1·000

TABLE XIV (b)

25°C

Solvent	Q cals.	- θ cals.	$-\Delta H_p$ cals.
Acetone	-	-260	7,920
CS_2	-	-670	7,510
Chloroform	-	+430	8,610
Ethyl Acetate	-	-140	8,040
Benzene	8,180	±0	8,180

TABLE XIV (c)

25°C

Solvent	ΔF_p	$-\Delta H_p$	$-T\Delta S_p$	$-\Delta S_p$
Acetone	2,910	7,920	10,830	36·3
CS_2	3,025	7,510	10,535	35·4
Chloroform	2,660	8,610	11,270	37·8
Ethyl Acetate	2,720	8,040	10,760	36·1
Benzene	2,695	8,180	10,875	36·5

TABLE XIV (d)

25°C

Solvent	$-\Delta F_c$	$-\Delta H_c$	$-T\Delta S_c$	$-\Delta S_c$
Acetone	4,460	7,605	3,145	10·5
CS_2	4,470	7,135	2,665	9·0
Chloroform	4,665	8,245	3,580	12·0
Ethyl Acetate	4,485	7,735	3,250	10·9
Benzene	4,565	7,810	3,245	10·9

TABLE XV (a)

Solute Carbon Disulphide

Solvent	p/N 25°C	p/p°N 25°C	RT log p/p°N 25°C	p/N 35°C	p/p°N 35°C
Acetone	1,293	3·601	+760·0	1,690	3·283
Benzene	553·1	1·541	+256·4	766·5	1·488
Chloroform	505·2	1·407	+202·7	704·4	1·368
CS_2	358·9	1·000	±0	515·0	1·000

TABLE XV (b)

25°C

Solvent	Q cals.	$-\theta$ cals. (calc.)	$-\Delta H_p$ cals. (calc.)
Acetone	-	-1,690	4,930
Benzene	-	-650	5,970
Chloroform	-	-535	6,085
CS_2	6,620	±0	6,620

TABLE XV (c)

25°C

Solvent	ΔF_p	$-\Delta H_p$	$-T\Delta S_p$	$-\Delta S_{p30°C.}$
Acetone	4,250	4,930	9,180	30·8
Benzene	3,745	5,970	9,715	32·6
Chloroform	3,690	6,085	9,775	32·8
CS_2	3,490	6,620	10,110	33·9

TABLE XV (d)

25°C

Solvent	$-\Delta F_c$	$-\Delta H_c$	$-T\Delta S_c$	$-\Delta S_{c30°C.}$
Acetone	3,125	4,615	1,490	5·0
Benzene	3,515	5,600	2,085	7·0
Chloroform	3,630	5,720	2,090	7·0
CS_2	4,005	6,245	2,240	7·5

TABLE XVI (a)

Solute Chloroform.

Solvent	p/N 25°C	p/p°N 25°C	RT log p/p°N 25°C	p/N 35°C	p/p°N 35°C
Acetone	129·0	0·648	-257·5	208·3	0·691
Benzene	164·3	0·825	-114·0	253·8	0·842
CS_2	288·7	1·450	+220·4	425·0	1·410
Diethyl Ether	77·67	0·390	-558·4	-	0·437 (Calc.)
Ethyl Acetate	112·9	0·567	-336·6	-	0·614 (Calc.)
Chloroform	199·1	1·000	±0	301·3	1·000

TABLE XVI (b)

25°C

Solvent	Q cals.	- θ cals.	$-\Delta H_p$ cals.
Acetone	-	+1,160	8,800
Benzene	-	+ 240	7,880
CS_2	-	- 580	7,060
Diethyl Ether	-	+2,015	9,655
Ethyl Acetate	-	+1,345	8,985
Chloroform	7,640	±0	7,640

TABLE XVI (c)

25°C

Solvent	ΔF_p	$-\Delta H_p$	$-T\Delta S_p$	$-\Delta S_p$
Acetone	2,880	8,800	11,680	39·2
Benzene	3,025	7,880	10,905	36·6
CS_2	3,360	7,060	10,420	35·0
Diether Ether	2,580	9,655	12,235	41·0
Ethyl Acetate	2,805	8,985	11,790	39·6
Chloroform	3,140	7,640	10,780	36·2

TABLE XVI (d)

25°C

Solvent	$-\Delta F_c$	$-\Delta H_c$	$-T\Delta S_c$	$-\Delta S_c$
Acetone	4,490	8,485	3,995	13·4
Benzene	4,235	7,510	3,275	11·0
CS_2	4,135	6,685	2,550	8·6
Diethyl ether	4,585	9,370	4,785	16·0
Ethyl Acetate	4,400	8,680	4,280	14·4
Chloroform	4,185	7,275	3,090	10·4

TABLE XVII (a)

Solute Diethyl Ether.

Solvent	p/N 25°C	p/p°N 25°C	RT log p/p°N 25°C	p/N 35°C	p/p°N 35°C	calc.
Benzene	151·9	0·283	-749·1	-	0·282	
CS_2	1,033	1·923	+387·8	-	1·828	
Chloroform	175·1	0·326	-664·6	-	0·366	
Ether	537·0	1·000	±0	775·5	1·000	

TABLE XVII (b)

25°C

Solvent	Q cals.	- θ cals.	$-\Delta H_p$ cals.
Benzene	-	-100	6,650
CS_2	-	-1,005	5,745
Chloroform	-	+2,110	8,860
Ether	6,750	±0	6,750

TABLE XVII (c)

25°C

Solvent	ΔF_p	$-\Delta H_p$	$-T\Delta S_p$	$-\Delta S_p$
Benzene	2,980	6,650	9,630	32·3
CS_2	4,115	5,745	9,860	33·1
Chloroform	3,065	8,860	11,925	40·0
Ether	3,730	6,750	10,480	35·2

TABLE XVII (d)

25°C

Solvent	$-\Delta F_c$	$-\Delta H_c$	$-T\Delta S_c$	$-\Delta S_c$
Benzene	4,280	6,280	2,000	6·7
CS_2	3,375	5,370	1,995	6·7
Chloroform	4,260	8,495	4,235	14·2
Ether	3,435	6,465	3,030	10·2

TABLE XVIII (a)

Solute Ethyl Acetate.

Solvent	p/N 25°C	p/p°N 25°C	RT log p/p°N 25°C	p/N 35°C	p/p°N 35°C
Benzene	100·6	1·076	+43·3	159·4	1·059
CS_2	230·2	2·462	+534·4	340·0	2·259
Chloroform	39·91	0·427	-504·8	71·66	0·476
Ethyl Acetate	93·50	1·000	±0	150·5	1·000

TABLE XVIII (b)

25°C

Solvent	Q cals.	- θ cals.	$-\Delta H_p$ cals.
Benzene	-	-160	8,480
CS_2	-	-1,565	7,075
Chloroform	-	+2,175	10,815
Ethyl Acetate	8,640	±0	8,640

TABLE XVIII (c)

25°C

Solvent	ΔF_p	$-\Delta H_p$	$-T\Delta S_p$	$-\Delta S_p$
Benzene	2,735	8,480	11,215	37·6
CS_2	3,225	7,075	10,300	34·6
Chloroform	2,185	10,815	13,000	43·6
Ethyl Acetate	2,690	8,640	11,330	38·0

TABLE XVIII (d)

25°C

Solvent	$-\Delta F_c$	$-\Delta H_c$	$-T\Delta S_c$	$-\Delta S_c$
Benzene	4,525	8,110	3,585	12·0
CS_2	4,270	6,700	2,430	8·2
Chloroform	5,135	10,450	5,315	17·8
Ethyl Acetate	4,515	8,335	3,820	12·8

The experimental results are summarised in Tables XIX to XXI.

ΔF, ΔH, $T\Delta S$ and θ are measured in kilocalories per mole solute. The entropy, ΔS, is given in calories per mole solute per degree.

Tables XXII (a), (b) and (c) are calculated from the solubilities given in Seidell's "Solubilities".

For these alkyl halides, p/N becomes p°/N_s, where p° is the vapour pressure of the pure solute at a given temperature, N_s its molar fraction in the (dilute) saturated solution. This is exact for a solid, and holds very well for nearly immiscible liquids.

$\Delta S_{p_{25^\circ}}$ is obtained from the temperature coefficient of the free energy, and $\Delta F_{p_{25^\circ}}$ is closely approximate to $\frac{1}{2}(\Delta F_{p_{20^\circ}} + \Delta F_{p_{30^\circ}})$.

$\Delta H_{p_{25^\circ}}$ can thus be found, and the functions are reduced to concentration units in Table XXII (c).

TABLE XIX.

25°C	Solvent Water		
Solute	$-\Delta F_c$	$-\Delta H_c$	$-T\Delta S_c$
MeOH	5·12	10·69	5·57
EtOH	5·02	12·33	7·31
n-PrOH	4·83	13·87	9·04
iso-PrOH	4·76	12·90	8·14
n-BuOH	4·72	15·39	10·68
iso-BuOH	4·53	14·69	10·16
sec-BuOH	4·62	14·51	9·89
tert-BuOH	4·52	13·89	9·37
n-AmOH	4·47	16·95	12·48
iso-AmOH	4·42	16·22	11·80
tert-AmOH	4·44	15·17	10·73
Acetone	3·92	9·44	5·52

ΔF_c, ΔH_c, and $T\Delta S_c$ in kilocalories/mole solute.

TABLE XX.

Summary.

Pressure Units		Solute					
Solvent		Acetone	Benzene	CS_2	Chloroform	Ether	EtOAc
		±0·00	+0·26	+1·69	-1·16		
Acetone	ΔF_p	3·22	2·91	4·25	2·88	-	-
	$-\Delta H_p$	7·58	7·92	4·93	8·80		
	$-\Delta S_p$	36·2	36·1	30·8	39·2		
		+0·31	±0·00	+0·65	-0·24	+0·10	+0·16
Benzene	ΔF_p	3·23	2·70	3·75	3·03	2·98	2·74
	$-\Delta H_p$	7·27	8·18	5·97	7·88	6·65	8·48
	$-\Delta S_p$	35·4	36·5	32·6	36·8	32·3	37·5
		+1·79	+0·67	±0·00	+0·58	+1·01	+1·57
CS_2	ΔF_p	4·03	3·03	3·49	3·36	4·12	3·23
	$-\Delta H_p$	5·79	7·51	6·62	7·06	5·75	7·08
	$-\Delta S_p$	32·6	35·1	33·9	35·0	33·1	34·8
		-1·92	-0·43	+0·54	±0·00	-2·11	-2·18
$CHCl_3$	ΔF_p	2·67	2·66	3·69	3·14	3·07	2·19
	$-\Delta H_p$	9·50	8·61	6·09	7·64	8·86	10·82
	$-\Delta S_p$	40·9	37·6	32·8	36·2	40·0	43·3
					-2·02	±0·00	
Ether	ΔF_p	-	-	-	2·58	3·73	-
	$-\Delta H_p$				9·66	6·75	
	$-\Delta S_p$				41·0	35·2	
			+0·14		-1·35		±0·00
EtOAc	ΔF_p	-	2·72	-	2·81	-	2·69
	$-\Delta H_p$		8·04		8·99		8·64
	$-\Delta S_p$		36·1		39·6		38·0

' ΔF_p, $-\Delta H_p$, in kilocalories/mole solute. $-\Delta S_p$ in cals/degree/mole solute.

TABLE XXI.

Summary.

Concentration Units		Solute: Acetone	Benzene	CS_2	Chloroform	Ether	EtOAc.
Solvent	$-\Delta F_c$	4·16	4·46	3·13	4·49		
Acetone	$-\Delta H_c$	7·27	7·61	4·62	8·49	-	-
	$-T\Delta S_c$	3·11	3·15	1·49	4·00		
	$-\Delta F_c$	4·03	4·57	3·52	4·24	4·28	4·53
Benzene	$-\Delta H_c$	6·90	7·81	5·60	7·51	6·28	8·11
	$-T\Delta S_c$	2·87	3·24	2·08	3·27	2·00	3·58
	$-\Delta F_c$	3·47	4·47	4·01	4·14	3·38	4·27
CS_2	$-\Delta H_c$	5·41	7·14	6·25	6·69	5·37	6·70
	$-T\Delta S_c$	1·94	2·67	2·24	2·55	1·99	2·43
	$-\Delta F_c$	4·66	4·67	3·63	4·19	4·26	5·14
$CHCl_3$	$-\Delta H_c$	9·13	8·25	5·72	7·28	8·50	10·45
	$-T\Delta S_c$	4·47	3·58	2·09	3·09	4·24	5·31
	$-\Delta F_c$				4·59	3·44	
Ether	$-\Delta H_c$	-	-	-	9·37	6·47	-
	$-T\Delta S_c$				4·78	3·03	
	$-\Delta F_c$		4·49		4·40		4·52
EtOAc	$-\Delta H_c$	-	7·74	-	8·68	-	8·34
	$-T\Delta S_c$		3·25		4·28		3·82

Units are kilocalories/mole solute.

TABLE XII (a)

Water Solvent

Solute	$\phi^{\circ}_{20°C.}$ mms.	$\phi^{\circ}_{30°C.}$ mms.	$\frac{\phi^{\circ}}{N_S}\times 10^{-2}$ 20°C.	$\frac{\phi^{\circ}}{N_S}\times 10^{-2}$ 30°C.	ΔF_{ϕ} 20°C.	ΔF_{ϕ} 30°C.	$-\Delta S_{\phi}$ 25°C.
PrCl	278·6	411·1	4,466	6,471	7,586	8,069	48·3
Iso PrCl	435·5	628·1	6,226	9,007	7,780	8,268	48·8
CH_2Cl_2	348·8	511·4	826	1,230	6,603	7,066	46·2
EtBr	386·0	546·0	2,558	3,690	7,261	7,729	46·8
PrBr	110·2	170·6	3,070	4,717	7,369	7,877	50·8
Iso PrBr	174·2	263·0	3,741	5,649	7,484	7,987	50·3
CH_2Br_2	34·7	56·4	292	463	5,995	6,479	48·4
MeI	331·4	483·4	1,842	2,668	7,069	7,534	46·5
EtI	108·5	167·5	2,332	3,495	7,207	7,696	48·9
PrI	33·9	54·6	299	500	7,352	7,912	56·0
Iso PrI	56·4	88·1	3,798	6,203	7,492	8,042	55·0

TABLE XXII (b)

Solute	ΔF_p	$-\Delta H_p$	$-T\Delta S_p$	$-\Delta S_p$
PrCl	7·830	6·565	14·395	48·3
Iso PrCl	8·025	6·515	14·540	48·8
CH_2Cl_2	6·835	6·965	13·800	46·3
EtBr	7·495	6·455	13·950	46·8
PrBr	7·625	7·515	15·140	50·8
Iso PrBr	7·735	7·255	14·990	50·3
CH_2Br_2	6·235	8·185	14·420	48·4
MeI	7·300	6·560	13·860	46·5
EtI	7·450	7·120	14·570	48·9
PrI	7·630	9·060	16·690	56·0
Iso PrI	7·765	8·630	16·395	55·0

TABLE XXII (c)

Solute	$-\Delta F_c$	$-\Delta H_c$	$-T\Delta S_c$	$-\Delta S_c$
PrCl	0·38	6·02	5·64	18·9
Iso PrCl	0·18	5·97	5·79	19·4
CH_2Cl_2	1·37	6·42	5·05	16·9
EtBr	0·71	5·91	5·20	17·4
PrBr	0·58	6·97	6·39	21·4
Iso PrBr	0·47	6·71	6·24	20·9
CH_2Br_2	1·97	7·64	5·67	19·0
MeI	0·91	6·01	5·10	17·1
EtI	0·76	6·57	5·81	19·5
PrI	0·58	8·51	7·93	26·6
Iso PrI	0·44	8·08	7·64	25·6

Units are kilocalories per mole solute

ΔS in calories per mole per degree.

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249. *The Solubility of Non-electrolytes. Part III. The Entropy of Hydration.*

By J. A. V. Butler and W. S. Reid.

It has been shown in previous papers (J., 1935, 280, 952) that the free energy of hydration of aliphatic compounds, evaluated as $\Delta F = RT \log p/N$, is to a considerable extent an additive property of the various groups in the molecule, indicating some kind of additive interaction between the parts of the molecule and the surrounding water. In the discussion of these data it was assumed provisionally that the heats of hydration of a series of compounds run parallel with the free energies of hydration, *i.e.*, that the entropies of hydration are not significantly different. An examination of the existing data, and some new measurements, shows that this is not the case, and it appears that the variation of the entropy of hydration is a predominant factor in determining the free energies of a series of similar compounds.

The heat of hydration which corresponds to the free energy given above is $\Delta H = H^\circ - H_g^\circ$, where H° is the partial heat content of the solute in an infinitely dilute solution and H_g° its heat content in the vapour at 1 mm. pressure. This can be determined practically as $\Delta H = Q - \lambda$, where Q is the heat of solution of the solute as pure liquid or solid in an infinitely dilute solution, and λ its heat of vaporisation at the same temperature. These data for a number of compounds, obtained in most cases from I.C.T., Vol. V, are given in Table I, together with the values of ΔF recorded in the previous papers. It can be seen that, as the number of CH_2 groups in a homologous series increases, the changes of ΔF and ΔH, instead of being parallel as was anticipated, are *in the opposite directions*. The entropy of hydration, which is given by $\Delta S = (\Delta H - \Delta F)/T$, therefore increases numerically by a considerable amount between one compound and its immediate homologue.

The entropy of hydration can also be obtained from the temperature coefficient of the free energy, by $d(\Delta F)/dT = -\Delta S$. In order to extend the table, which was very incomplete in its original form, ΔS has been obtained for a number of compounds by determining ΔF at 25° and 35°. These results are marked * in the table.

Table I.

Entropy of Hydration of some Aliphatic Compounds.†

	$Q_{25°}$.	$\lambda_{25°}$.	$-\Delta H_{25°}$.	$\Delta F_{25°}$.	$\Delta F_{35°}$.	$-T.\Delta S$.	$-\Delta S$.
A. Aliphatic alcohols.							
Methyl	−2·0	9·24	11·24	3·09	—	14·33	48
Ethyl	−2·55	10·33	12·88	3·19	—	16·07	54
n-Propyl	−3·05	11·37	14·42	3·38	—	17·80	60
*iso*Propyl	−3·77	9·68	13·45	3·45	—	16·90	56
n-Butyl *	—	12·63	—	3·49	4·14	—	65
*iso*Butyl	−2·90	12·34	15·24	3·68	—	18·92	63
sec.-Butyl *	—	12·00	—	3·59	4·22	—	63
tert.-Butyl	−3·24	11·20	14·44	3·69	—	18·13	61
n-Amyl *	—	13·60	—	3·73	4·44	—	71
tert.-Amyl *	—	11·96	—	3·77	4·43	—	65
B. Other compounds.							
Ethylamine	−6·33	6·58	12·91	3·58	—	16·49	55
Ethyl acetate	−3·07	8·64	11·71	5·11	—	16·82	56
Acetone	−2·51	7·58	10·09	4·29	—	14·38	48
Acetone *	—	—	—	4·29	4·76	—	48
Glycerol	−1·51	23·22	24·73	−1·01	—	23·72	80
Glycerol *	—	—	—	−1·01	−0·21	—	80
Chloroform	−2·20	7·64	9·84	7·14	—	16·98	57

† Units in all columns except the last are kg.-cals.; ΔS is in cals./degree.

The solubility of gases is often expressed by the Ostwald coefficient $\gamma = c_l/c_g$, where c_l and c_g are the concentrations in mols./c.c. in the liquid and the vapour. In these units the free energy of hydration is $\Delta F_c = -RT \log \gamma$, and since for sufficiently dilute solutions

$p/N = 1{\cdot}7032 \times 10^7 Td/273{\cdot}1M_1$, where M_1 is the molecular weight and d the density of the solvent, it follows that the entropy of solution when these units of concentration are used is greater than that on the p/N system by 29·4 units at 25°, *i.e.*, $\Delta S_{(p/N)} + 29{\cdot}4 = \Delta S_{(c)}$. Table II gives the entropy of solution of a number of gases calculated from the solubility data.

TABLE II.

Entropy of Hydration of some Gases (in cals./degree at ca. 25°).

	$-\Delta S_{(p/N)}$.		$-\Delta S_{(p/N)}$.		$-\Delta S_{(p/N)}$.		$-\Delta S_{(p/N)}$.
He.....	40·0 [1] (38·6) [2]	Rn	47·5 [1]	CO	43·0	C_2H_6	48·6
Ne.....	42·0 [1] (39·4) [2]	H_2	39·2 [3]	CO_2	43·8	C_2H_4	44·5
A	43·4 [1] (43·1) [2]	N_2	43·0	COS	48·3	C_2H_2	38·8
Kr.....	45·5 [1]	O_2	44·5	CH_4	45·0	CH_3Cl	46·8
Xe.....	46·8 [1]						

[1] From Valentiner's interpolation formulæ (*Z. Physik*, 1927, **42**, 253).
[2] Data from Lannung (*J. Amer. Chem. Soc.*, 1930, **52**, 73).
[3] Remainder from I.C.T., Vol. IV.

EXPERIMENTAL.

The methods used for the determination of the temperature coefficient of p/N were similar to those previously described, but a more efficient six-bulb bubbler was employed to saturate the gas. The experimental figures are given in Table III, where N is the molar fraction of the solute in the original solution and x its weight % in the condensate. The measurements at 25° were repeated to secure uniformity with those at 35° and, except in the case of glycerol, are in good agreement with the figures recorded previously.

TABLE III.

Temperature Coefficients of the Partial Pressures.

		$T = 25°$.			$T = 35°$.			
	$N \times 10^3$.	x.	p/N.	ΔF_{25}, mean.	x.	p/N.	ΔF_{35}, mean.	$-\Delta S_{30°}$.
n-Butyl	1·108	6·43	359		8·50	861		
alcohol	1·108	6·45	360		8·52	863		
	0·863	5·17	366	3490	6·79	866	4145	65
sec.-Butyl	0·821	5·71	427		7·19	969		
alcohol	0·821	5·69	425		7·18	968		
	0·821	5·69	425	3590	7·18	968	4220	63
n-Amyl	0·413	4·39	541		6·30	1400		
alcohol	0·413	4·37	537		6·29	1400		
	0·397	4·29	549	3730	6·19	1430	4440	71
tert.-Amyl	1·087	11·49	581		14·7	1380		
alcohol	1·087	11·47	578		14·7	1360		
	1·087	11·44	577	3770	14·6	1355	4430	65
Acetone	0·822	13·3	1380		13·0	2380		
	0·822	13·1	1360		13·0	2380		
	0·822	13·5	1400	4290	12·9	2370	4770	48
Glycerol	10·74	0·042	0·182		0·091	0·71		
	10·74	0·040	0·173		0·091	0·69		
	10·74	0·043	0·188	−1010	0·093	0·71	−213	80

DISCUSSION.

On the whole, the entropies of solution are strikingly independent of the chemical nature of the solute. This can be illustrated by the following examples :

C_2H_6.			$CH_3{\cdot}OH$.			CH_3Cl.		
$-\Delta H$.	ΔF.	$-\Delta S$.	$-\Delta H$.	ΔF.	$-\Delta S$.	$-\Delta H$.	ΔF.	$-\Delta S$.
4·43	10·05	49	11·24	3·09	48	6·30	7·65	47

Methyl alcohol, ethane, and methyl chloride all have nearly the same entropy of solution although their heats of solution and solubilities differ greatly. Although there do appear to be some minor constitutive effects, the entropy of solution seems to be mainly a function of the size of the solute molecule; *e.g.*, in the inert gases the entropy of solution increases from helium to radon. In a homologous series there is an increase of about 5 units in

$-\Delta S$ for each additional CH_2 group. This has a most important effect on the solubility of these compounds. If the entropy were a constant, the solubility of the vapour (N/p) would be determined by the heat of solution and would *increase* as the number of carbon atoms increased. The decrease in this ratio, which actually occurs and is one of the factors which produce the steady decrease of solubility of the *liquid* in going up the series, is due to this property of the entropy.

The origin of this effect is not obvious. If the entropy change on solution depends mainly on the size of the solute molecule it is reasonable to suppose that it is associated with the size of the cavity in the water which is required to hold it. Water is an abnormal liquid and its entropy of vaporisation is about 5 units less than that of a liquid which obey's Trouton's rule. This difference is due to orientational effects. Now at first sight we might expect that the introduction of solute molecules would tend to upset the orientation of the water molecules and therefore cause an increase in their entropy which might well be proportional to the size of the solute molecule. If this were the case the partial entropy of the solute in aqueous solution would be greater than its normal entropy in the dissolved state, and the decrease of entropy on solution would diminish as the size of the solute molecule increased.

This argument is, however, fallacious. The entropy of a system is a measure of the number of possible configurations having the given entropy, *i.e.*, of the probability of the given state. The entropy of water is abnormally low because the average energy at a given temperature corresponds to a certain degree of orientation, which decreases the probability of this state. The presence of molecular cavities within the liquid may also make the degree of orientation, which is required by the average energy, more improbable and therefore decrease the entropy. The partial entropy of the solute will then be abnormally low. The observed effect can thus be accounted for on the hypothesis that the solute molecules have a disorientating influence on the water, which increases with the size of the solute molecules. But it is important to notice that what is postulated is not so much an actual decrease in orientation, which would influence the energy of solution, as in the probability of an orientated state. If these conclusions are correct, the partial entropies of solutes in other " associated " liquids should also be abnormally small.

SUMMARY.

The entropies of hydration of a number of substances have been calculated from the heats and free energies of hydration, or determined from the temperature coefficient of the free energy. This quantity is little influenced by the constitution of the solute molecule, but it appears to be mainly dependent on its size. It is suggested that the solute molecules have a disorientating effect on water, increasing with their size, which gives the solute an abnormally low partial entropy in the solution.

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D I S C U S S I O N

(a) Water Solutions.

(1) Pressure Scale.

Though the results given in Tables III and XII were discussed by Butler in a Paper to the Faraday Society (Butler, Trans. Farad. Soc., 33, 1, 229, 1937) the main points may be repeated here.

A comparison of columns 5 and 6 in Table XII (a) shows that, while RT log p/N, or ΔF_p, increases regularly as the homologous series of alcohols is ascended, RT log p/p°N values show no such regularity. So that it is preferable to refer the free energy of hydration to the gaseous state as standard, as in RT log p/N, and not to the complex liquid state, which is the reference standard in the case of RT log p/p°N values.

The heat of hydration, ΔH_p, also varies by regular increments from one homologue to the next, but in the reverse direction to ΔF_p.

The entropy of hydration, ΔS_p, thus varies considerably on ascending the alcohol series.

If the entropy were constant, the vapour solubility,

N/p, would increase from one normal alcohol to a higher alcohol, instead of decreasing, so the entropy change has an important effect on the solubility of the alcohol vapours in water.

As the homologous series of alcohols is ascended, ΔF_p increases by equal increments (160 calories); ΔH_p shows a regular decrease (1,565 calories); and the decrease for each stage in ΔS_p is 6·0 calories per degree centigrade; so that a linear relationship exists between all three quantities. In the above-mentioned paper, $-\Delta H_p$, plotted against $-\Delta S_p$, gives a straight line which includes all of the alcohols listed in Table XII. The same relationship exists for gases in water, but the straight lines are non-coincident.

Since the number of possible configurations of a system having a given energy determines its entropy, a solute molecule may reduce the number of admissible configurations, thus decreasing the entropy. And the results would be explained if this effect were proportional to the interaction energy between solute and solvent. Conversely, the solvent molecules surrounding a solute molecule would be similarly affected, and any entropy change arising from this effect would decrease the partial entropy of the solute.

Bell's explanation (Bell, Trans. Farad. Soc., 33, 496, 1937) is that within this group of alcohol molecules the relative importance of dipole and dispersion

forces is roughly constant; this is reasonable, for with small molecules containing the hydroxyl group, dipole forces should be important factors.

Whatever the origin of the effect, those groups, such as hydroxyl groups, which form "hydrogen bonds" give rise to a new factor. This factor has the effect that non-polar compounds having the same heat of hydration as polar compounds, yet have a lesser entropy of hydration.

It might be expected that the entropy would be a function of the partial molar volume. These values, given in Table A, were calculated for 20°C by Dr. W. J. C. Orr of this Department from the data of Bernar and Rüber where $\mathring{V}$ is the molar volume in ccs., $\bar{\mathring{V}}$ the partial molar volume. Since the entropy varies but little with temperature, the results are comparable, and are graphed in Figure A, which shows that an approximate linear relationship does exist for the alcohol series.

Figure A

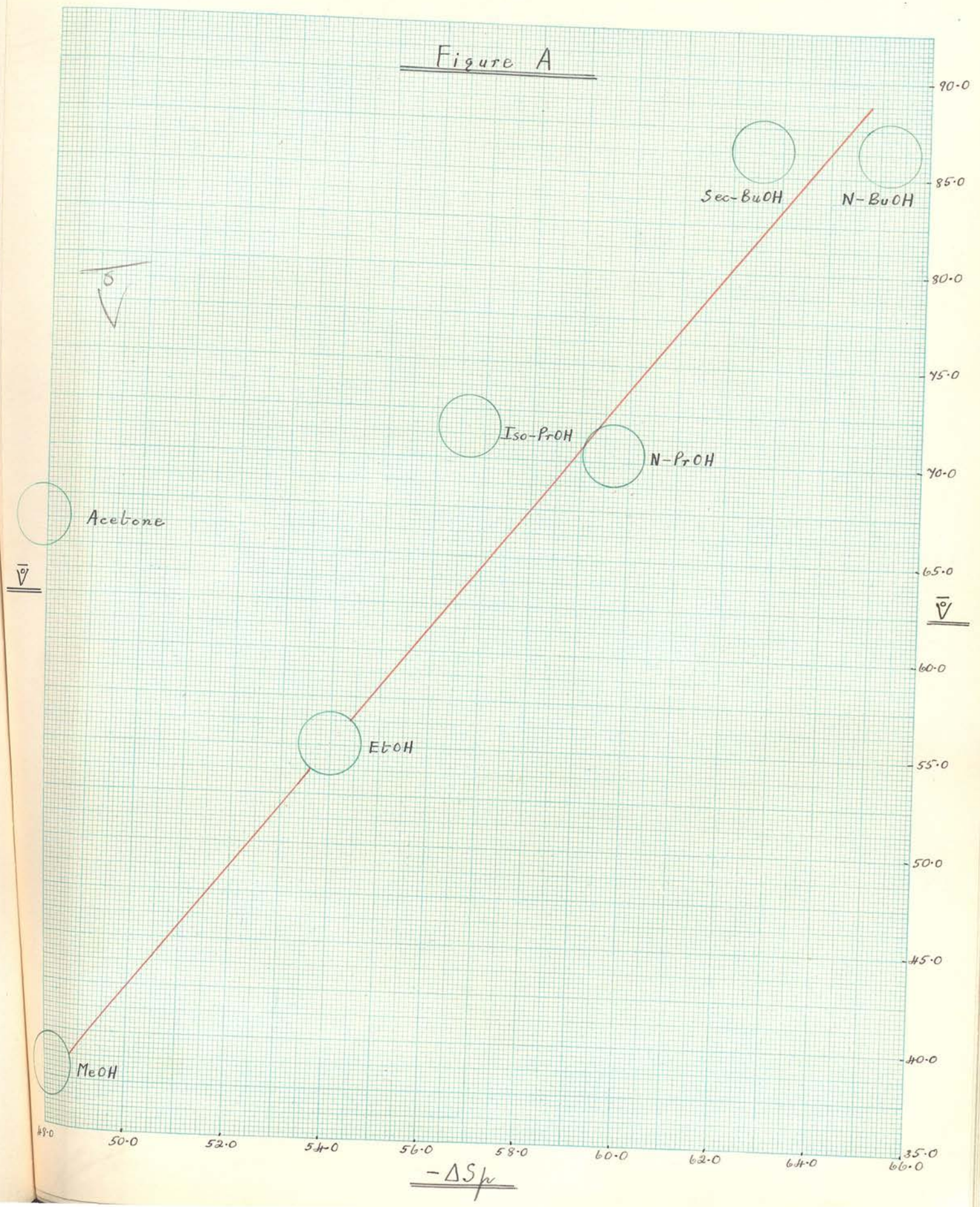

90·0
85·0
80·0
75·0
70·0
65·0
60·0
55·0
50·0
45·0
40·0
35·0
$\bar{V}$
$\bar{V}$
Sec-BuOH
N-BuOH
Iso-PrOH
N-PrOH
Acetone
EtOH
MeOH
48·0
50·0
52·0
54·0
56·0
58·0
60·0
62·0
64·0
66·0
$-\Delta S_v$

TABLE A.

Solute	Density 20°/4°	$\mathring{V}$ ccs. 20°C	$\bar{\mathring{V}}$ ccs. 20°C	$-\Delta S_p$ 25°C
MeOH	0·7958 (15°C)	40·25	38·11	48·2
EtOH	0·7893	58·33	55·07	54·0
n-PrOH	0·8036	74·74	70·45	59·7
Iso-PrOH	0·7851	76·51	71·68	56·7
n-BuOH	0·8098	91·48	86·28	65·2
Sec-BuOH	0·8065	91·85	86·33	62·6
Glycerol	1·2609	73·01	70·59	80·0
Acetone	0·7920 (19·8°C)	73·29	66·41	47·9

Latimer and Buffington (J.A.C.S., 48, 2297, 1926) have shown that, for gaseous ions also, there exists a linear relationship between the entropy and heat of solution.

(2) Concentration Scale.

In order to facilitate comparison with the results for the organic solutions, the heat, free energy and entropy of hydration have been reduced to concentration units in Table XIX.

Figures B and C show the relationships between ΔF_c and $T\Delta S_c$ for (a) the alcohol series and for (b) the alkyl halides given in Table XXII (c).

In Figure B, all of the alcohols lie on the same

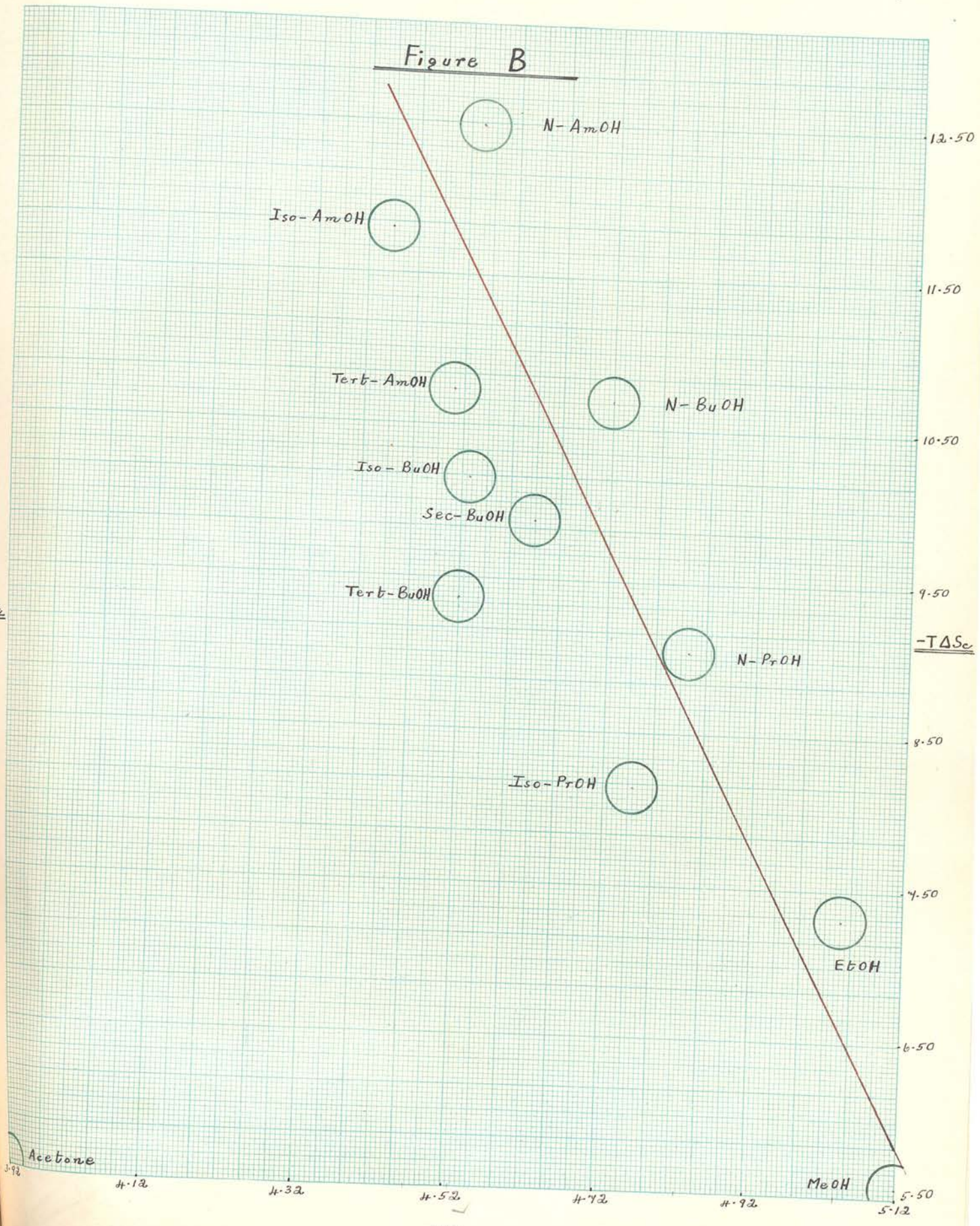
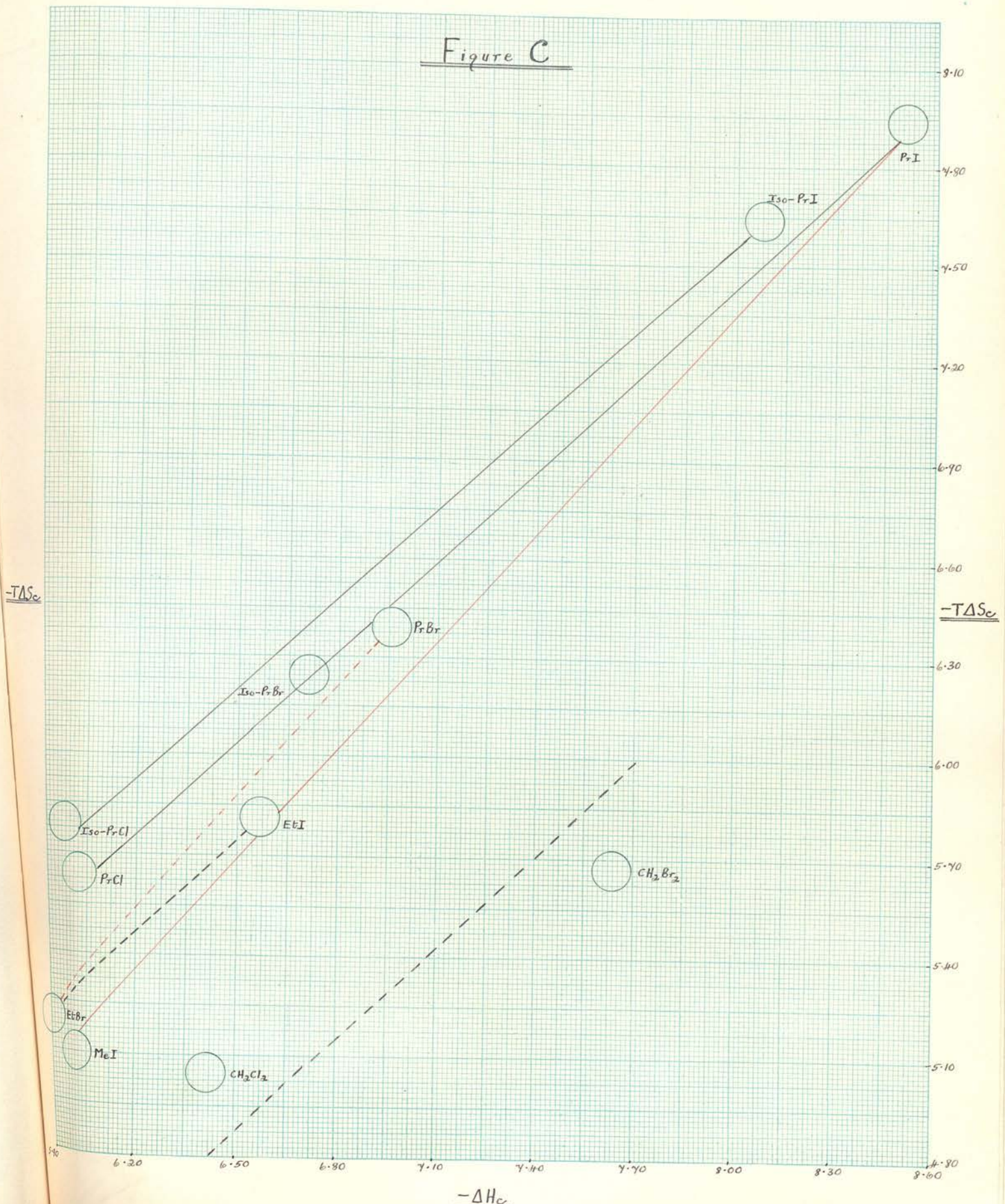


Figure B
N-AmOH
Iso-AmOH
Tert-AmOH
N-BuOH
Iso-BuOH
Sec-BuOH
Tert-BuOH
N-PrOH
Iso-PrOH
EtOH
MeOH
Acetone
12.50
11.50
10.50
9.50
8.50
7.50
6.50
5.50
5.12
4.92
4.12
4.32
4.52
4.72
4.92
-TΔSc
-TΔSc
-ΔFc

Figure C


-TΔSc
-TΔSc
-ΔHc
PrI
Iso-PrI
PrBr
Iso-PrBr
Iso-PrCl
PrCl
EtI
EtBr
MeI
CH2Br2
CH2Cl2
9·10
9·00
8·90
8·80
8·70
8·60
8·50
8·40
8·30
8·20
8·10
8·00
7·90
7·80
7·70
7·60
7·50
7·40
7·30
7·20
7·10
7·00
6·90
6·80
6·70
6·60
6·50
6·40
6·30
6·20
6·10
6·00
5·90
5·80
5·70
5·60
5·50
5·40
5·30
5·20
5·10
5·00
4·90
4·80
6·20
6·50
6·80
7·10
7·40
7·70
8·00
8·30
8·60

straight line.

In Figure C, there are two relationships. (1) As in the alcohol series, MeI, EtI and PrI lie on the same line, but the isomer, iso PrI apparently does not.

(2) A series with the same alkyl group shows a linear relationship eg. (a) PrCl, PrBr, PrI

(b) Iso PrCl, Iso PrBr, Iso PrI.

Again, as with the alcohol homologues, RT log p/N increases by about 160 calories for each additional $-CH_2$ group, so that the increment seems independent of the radical attached to the alkyl group.

(b) Organic Solvents.

As Butler (Butler and Harrower, Trans. Farad. Soc., 33, 189, 1937) has already shown that the main forces between solute and solvent molecules in such solutions are the van der Waals or Dispersion Forces, even where the solute has a polar character, we will discuss only the relationships between the various thermodynamic quantities. The fullest interpretation of the separate results is given by Hildebrand's "Internal Pressure" Theory.

(1) Pressure Scale.

In the results discussed above, the deviation from Raoult's Law is universally positive. With organic mixtures, both types of deviation occur, as shown in Table B, where the $p/p^{\circ}N$ values are listed at 25°C and 35°C.

TABLE B

Solvent	p/p°N (25°C)	p/p°N (35°C)	Solute
Acetone	1·00	1·00	
Benzene	1·02	1·00	Acetone
CS_2	3·89	3·51	
Chloroform	0·39	0·44	
Benzene	1·00	1·00	
Acetone	1·44	1·41	
CS_2	1·74	1·67	Benzene
Chloroform	0·94	0·96	
EtOAc	1·04	1·03	
CS_2	1·00	1·00	
Acetone	3·60	3·28	Carbon Disulphide
Benzene	1·54	1·49	
Chloroform	1·41	1·37	
Chloroform	1·00	1·00	
Acetone	0·65	0·69	
Benzene	0·83	0·84	
CS_2	1·45	1·41	Chloroform
Ether	0·39	0·44	
EtOAc	0·57	0·61	
Ether	1·00	1·00	
CS_2	1·92	1·83	Diethyl Ether
Chloroform	0·33	0·37	
EtOAc	1·00	1·00	
Benzene	1·08	1·06	Ethyl Acetate
CS_2	2·46	2·26	
Chloroform	0·43	0·48	

The table shows that the components of any given system both show positive or negative deviations. Rarely do positive and negative deviations appear simultaneously. A notable exception is the case of water-pyridine mixtures, discovered by Bronsted (Z. physik. Chem., 68, 693, 1910).

Again, for the above solutions, $p/p^{\circ}N$ approaches more nearly to unity with rise in temperature, so that the solutions become more ideal at higher temperatures.

If we consider the signs of the quantities $\Delta H^{\circ}_p - \Delta H_p$, $\Delta F_p - \Delta F^{\circ}_p$, and $\Delta S_p - \Delta S^{\circ}_p$, a further regularity appears. Table C gives the first two quantities in calories, the third in calories per degree. ΔF°_p, ΔH°_p, ΔS°_p, are the values of the free energy, heat and entropy of vaporisation of the pure liquids, which are given in Table XI. Since ΔF°_p is RT log p°, $\Delta F_p - \Delta F^{\circ}_p$ is RT log $p/p^{\circ}N$, which is a convenient quantity to use, as its sign is that of the Raoult's Law Deviation. $\Delta H^{\circ}_p - \Delta H_p$ is θ_{∞}, the heat of solution of the liquid solute in an infinite amount of solvent. And $\Delta S_p - \Delta S^{\circ}_p$ is the entropy of solution of the liquid solute.

TABLE C.

Solvent	$\Delta H^\circ - \Delta H$ (θ_∞)	$\Delta F - \Delta F^\circ$ (RT log p/p°N)	$\Delta S - \Delta S^\circ$	Solute
Acetone	±0	±0	±0	
Benzene	+ 310	+ 10	+ 0·8	
CS_2	+ 1,795	+ 805	+ 3·6	Acetone
Chloroform	- 1,915	- 555	- 4·7	
Benzene	±0	±0	±0	
Acetone	+ 260	+ 215	+ 0·4	
CS_2	+ 670	+ 330	+ 1·4	Benzene
Chloroform	- 430	- 40	- 1·1	
EtOAc	+ 140	+ 25	+ 0·4	
CS_2	±0	±0	±0	
Acetone	+ 1,690	+ 760	+ 3·1	Carbon Disulphide
Benzene	+ 650	+ 255	+ 1·3	
Chloroform	+ 535	+ 200	+ 1·1	
Chloroform	±0	±0	±0	
Acetone	- 1,160	- 260	- 3·0	
Benzene	- 240	- 145	- 0·6	
CS_2	+ 580	+ 220	+ 1·2	Chloroform
Ether	- 2,015	- 560	- 4·8	
EtOAc	- 1,345	- 335	- 3·4	
Ether	±0	±0	±0	
CS_2	+ 1,005	+ 385	+ 2·1	Diethyl Ether
Chloroform	- 2,110	- 665	- 4·8	
EtOAc	±0	±0	±0	
Benzene	+ 160	+ 45	+ 0·4	Ethyl Acetate
CS_2	+ 1,565	+ 535	+ 3·4	
Chloroform	- 2,175	- 505	- 5·6	

It is seen that the three columns always bear the same sign. The first and last columns show a quantitative agreement irrespective of sign, solute or solvent.

Thus, for these solutions, there is a parallelism between the deviations from ideality and the entropies and heats of solution. Butler (J.A.C.S., 47, 1, 1925) showed that, for certain dilute amalgams, e.g. for thallium and mercury in thallium amalgams, the deviations from Raoult's Law expressed as log $p/p^{\circ}N$ are proportional to the partial heats of solution.

The explanation is that, if a system absorbs heat, the energy absorbed will give rise to an increase in the partial vapour pressures of the components, and so lead to a positive deviation. The reverse holds when $p/p^{\circ}N$ is less than unity.

Fig. D shows the relationship between the entropies of solvation and the heats of solution, θ, for a series of solutes.

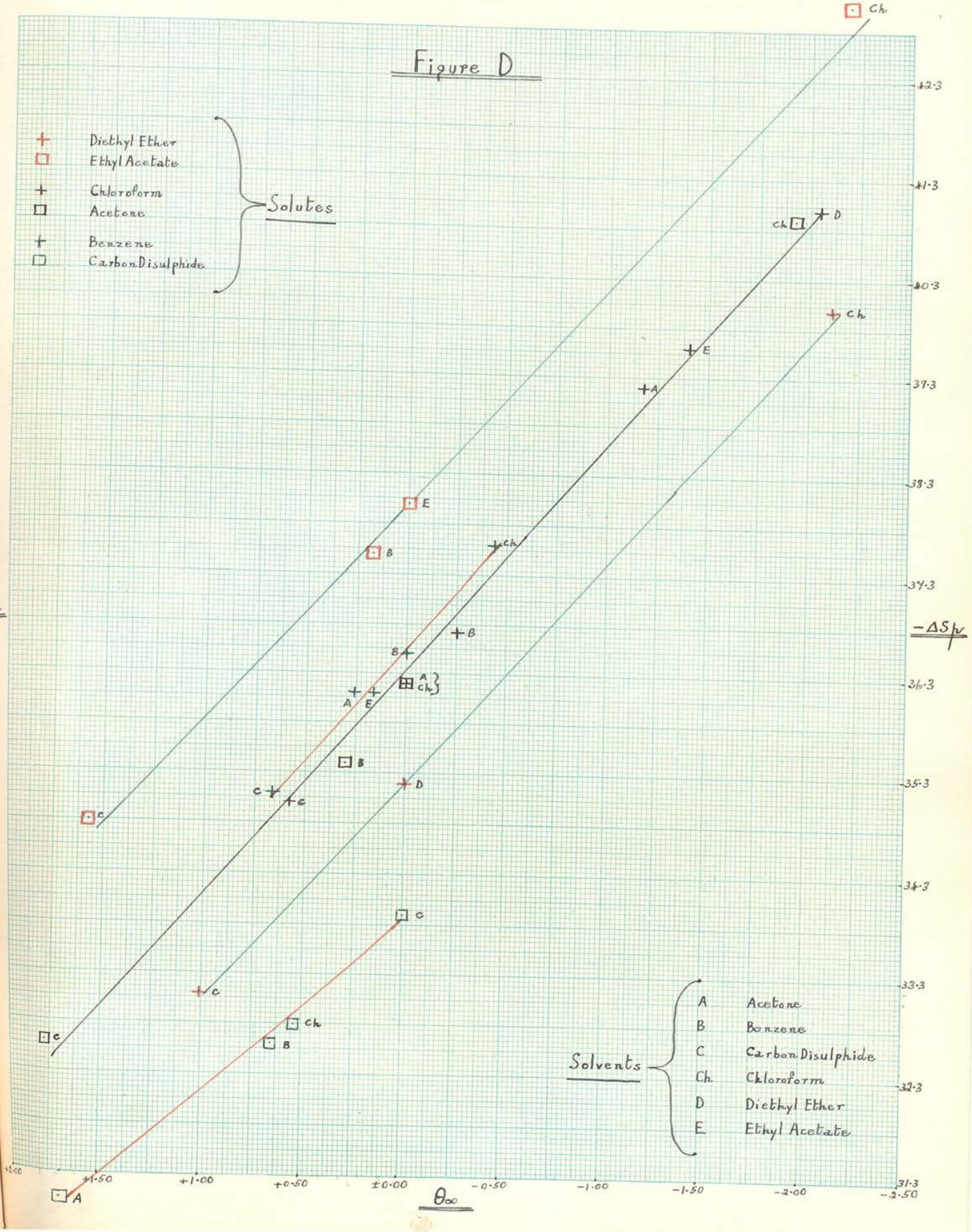
Each solute has its own line passing through the point occupied by the pure liquid solute itself.

The conclusion is that any heat effect on mixing has a proportional effect on the entropies of the components of a system.

For systems where the components are non-polar or nearly so, Hildebrand (J.A.C.S., 51, 66, 1929) proposed the equation

$$\bar{F}_2 - \bar{F}_2^{\circ} = RT \log N_2 - \alpha N_1^2$$

Figure D


Diethyl Ether
Ethyl Acetate
Chloroform
Acetone
Benzene
Carbon Disulphide
Solutes
-ΔSv
-ΔSv
θ∞
+1·50
+1·00
+0·50
±0·00
-0·50
-1·00
-1·50
-2·00
-2·50
42·3
41·3
40·3
39·3
38·3
37·3
36·3
35·3
34·3
33·3
32·3
31·3
A Acetone
B Benzene
C Carbon Disulphide
Ch. Chloroform
D Diethyl Ether
E Ethyl Acetate
Solvents

where $\bar{F}_2^\circ$ = molar free energy in the pure liquid,

$\bar{F}_2$ = molar free energy in the solution

N_1 and N_2 are the molar fractions of the components,

and α is a constant for a given mixture at a given temperature.

The constant α gives a measure of the deviation of a system from Raoult's Law.

Those solutions which obey the equation Hildebrand terms "regular solutions" and these have no chemical effects and no orienting effects, i.e. the entropy of solvation, for a given solute in these solutions is constant, and identical with the entropy of the pure solute.

Thus "regular solutions" provide a special case of the relation shown graphically in Fig. D.

(2) Concentration Scale.

We will now consider the relationships that exist between the various thermodynamic functions when the results are evaluated in terms of the Ostwald Coefficient.

Relation A; Evans and Polanyi, (Trans. Farad. Soc., 33, 1333, 1936) showed that, for a given solute in a series of non-polar solvents, a linear relationship exists between the entropies and heats of solvation; they give this relation in the form

$$\Delta S/R = \rho \Delta H + c,$$

where ρ and c are constants, and R is the gas constant.

Relation B; Bell showed that there is a linear relationship between the heats and entropies of solvation for a series of gases in a non-polar solvent; and that the converse for these solutes, relation A, does not hold.

For benzene in particular, the gas line is coincident with the line given by the first four normal aliphatic alcohols, whose free energies were measured by Harrower at 25°C. Cf. Butler and Harrower, (loc. cit.).

Bell, discussing both relations, suggests that the relative size of the solute molecule is the predominating factor. Relation A will be true when the solute molecules are even slightly larger than those of the solvent. And Relation B will hold when the solute molecules are definitely smaller than the solvent molecules.

Neither or both relations, Bell suggests, should hold where solute and solvent molecules do not differ greatly in size. The present experiments, where completely miscible liquids are used, fulfil this condition. The results, taken from Table XXI, are graphed in Figure E.

It seems to the author that either, none, or both relations are possible.

For A holds when the solute molecules are even

slightly larger than the solvent molecules; so that, when the solute molecules are the same size as, or even when slightly less than the solvent molecules, the relation may be expected to hold at least approximately.

Thus, relation A may well be universally true for the solutions under consideration, but B may hold only in certain cases.

Figure E shows that, of the two relations, only A holds universally. Each solute line passes through that point given by the pure solute itself.

But, in the case of relation B, there are three striking exceptions. Solute benzene does not lie on the solvent lines for acetone and chloroform, nor on its own solvent line.

And so, while Relation A, in the main, holds very well, Relation B does not seem to be universally true.

There are, therefore, various linear relationships between the different thermodynamic functions for both polar and non-polar solvents. For convenience, these various relationships are now quoted in brief.

There are Linear Relationships

(1) Between ΔH, ΔF and ΔS for the lower aliphatic alcohols in solvent water. (Pressure and Concentration Scales); a similar relationship exists for a series of alkyl halides in water.

(2) Between ΔH, ΔF, and ΔS for a series of gases in

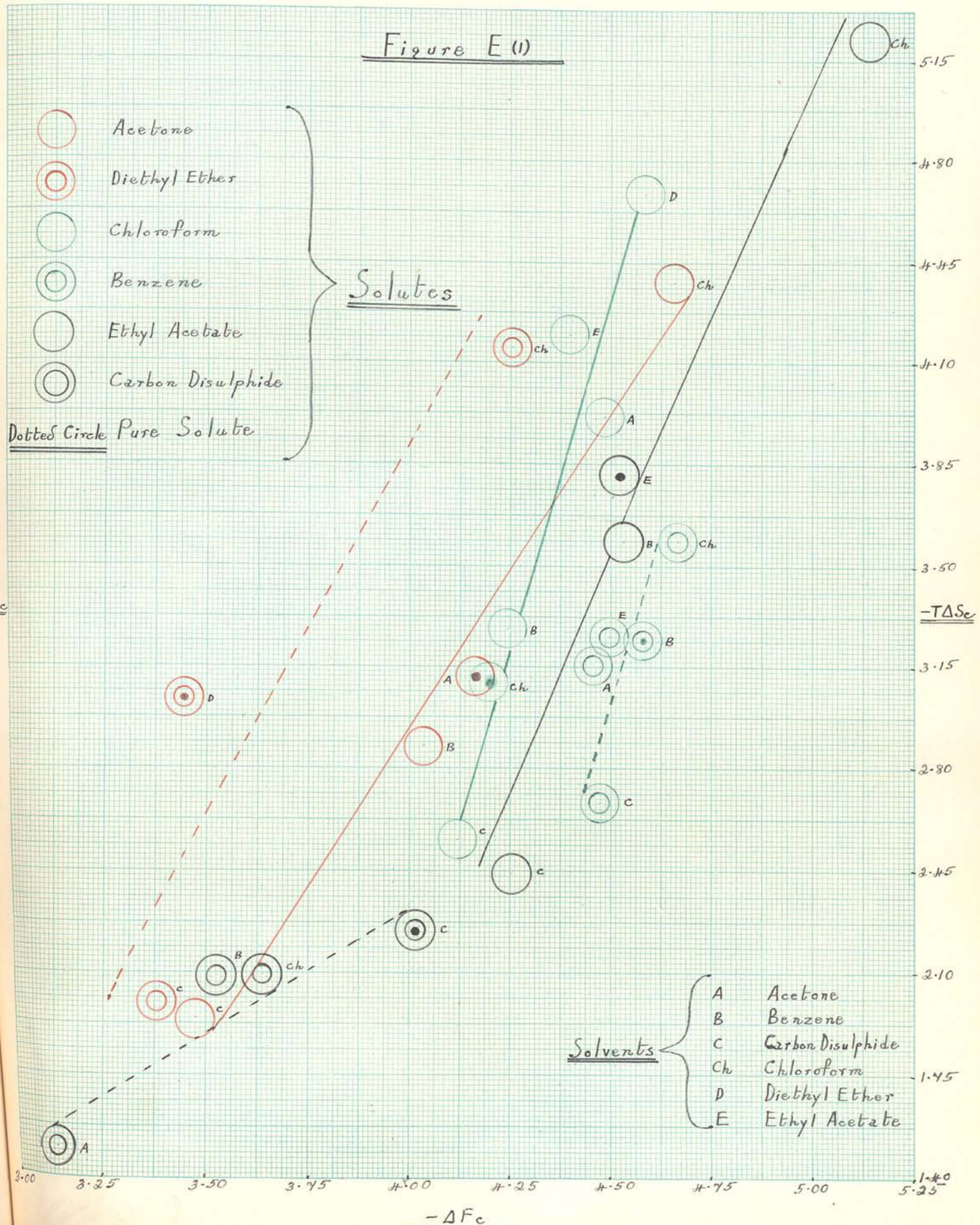
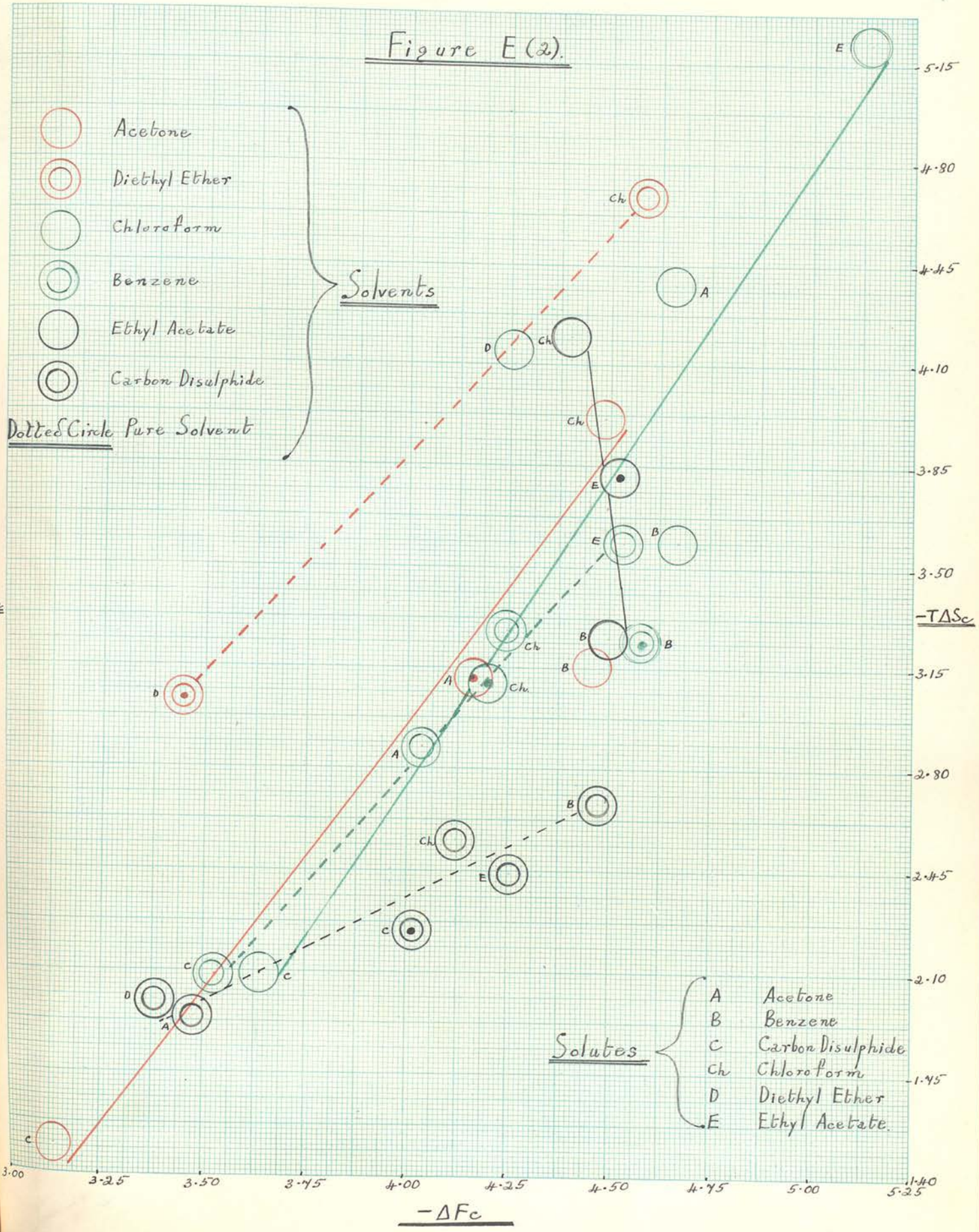


Figure E (1)
Acetone
Diethyl Ether
Chloroform
Benzene
Ethyl Acetate
Carbon Disulphide
Solutes
Dotted Circle Pure Solute
-TΔSc
-ΔFc
Solvents
A Acetone
B Benzene
C Carbon Disulphide
Ch Chloroform
D Diethyl Ether
E Ethyl Acetate
3·00
3·25
3·50
3·75
4·00
4·25
4·50
4·75
5·00
5·25
1·40
1·45
2·10
2·45
2·80
3·15
3·50
3·85
4·10
4·45
4·80
5·15

Figure E (2).


Acetone
Diethyl Ether
Chloroform
Benzene
Ethyl Acetate
Carbon Disulphide
Solvents
Dotted Circle Pure Solvent
-TΔSc
-ΔFc
5·15
4·80
4·45
4·10
3·85
3·50
3·15
2·80
2·45
2·10
1·45
1·40
3·00
3·25
3·50
3·75
4·00
4·25
4·50
4·75
5·00
5·25
Solutes
A Acetone
B Benzene
C Carbon Disulphide
Ch Chloroform
D Diethyl Ether
E Ethyl Acetate

water (Pressure and Concentration Scales.).

(3) Between ΔH, ΔF, and ΔS for gaseous ions in water (Pressure and Concentration Scales.).

(4) Between θ_∞ and ΔS for each solute in a series of organic solvents (Pressure Scale).

(5) Between ΔH, ΔF and ΔS for a series of gases in organic solvents. In particular, in benzene, the normal aliphatic alcohols (C_1 to C_4) lie on this line. (Pressure and Concentration Scales)

(6) Between ΔH, ΔF and ΔS for each solute in a series of organic solvents. (Concentration Scale) and (7) Between ΔH, ΔF and ΔS for a series of solutes in a non-polar solvent. (Concentration Scale). Relations (6) and (7), in the main, hold simultaneously for the solutions considered. In (4), (6) and (7), the same solutions are under consideration.

SUMMARY.

(1) An efficient method has been devised for the determination of the free energy of solvation referred to the vapour as standard state (RT log p/N) or to the liquid (RT log p/p°N) as reference standard.

(2) The entropy of solvation has been evaluated by measuring RT log p/N at two temperatures (25°C and 35°C).

(3) The partial vapour pressures, at 25°C and 35°C, have been measured for some aliphatic alcohols in water; and for acetone, benzene, carbon disulphide, chloroform, diethyl ether and ethyl acetate in each other.

(4) The free energy, heat and entropy of solvation have been calculated (a) with reference to the vapour at unit pressure (1 mm. Hg) (b) in terms of the Ostwald Coefficient.

(5) Linear relationships between the three thermodynamic functions are found for the alcohol and alkyl halide series in water.

(6) The entropy variations are related to the partial molar volumes for the alcohol series.

(7) Linear relationships, named A and B heretofore, exist, for the organic solutions, between the functions, evaluated in concentration units; and the relative size of the solute molecule is considered the main factor in these cases.

In conclusion, I thank Dr. J. A. V. Butler for his helpful criticisms throughout these researches, and the Moray Fund for a grant towards the purchase of instruments and materials.